

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION
(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

United States Patent and Trademark
Office
(Box PCT)
Crystal Plaza 2
Washington, DC 20231
ÉTATS-UNIS D'AMÉRIQUE

in its capacity as elected Office

Date of mailing: 22 October 1998 (22.10.98)	
International application No.: PCT/FI98/00329	Applicant's or agent's file reference: NEST 74 PCT
International filing date: 14 April 1998 (14.04.98)	Priority date: 11 April 1997 (11.04.97)
Applicant: KOISTINEN, Jari et al	

1. The designated Office is hereby notified of its election made:

in the demand filed with the International preliminary Examining Authority on:

24 September 1998 (24.09.98)

in a notice effecting later election filed with the International Bureau on:

2. The election was

was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer: J. Zahra Telephone No.: (41-22) 338.83.38
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PARENT COOPERATION TREAT

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**NOTIFICATION OF THE RECORDING
OF A CHANGE**

(PCT Rule 92bis.1 and
Administrative Instructions, Section 422)

Date of mailing (day/month/year) 23 September 1999 (23.09.99)			
Applicant's or agent's file reference NEST 74 PCT		IMPORTANT NOTIFICATION	
International application No. PCT/FI98/00329		International filing date (day/month/year) 14 April 1998 (14.04.98)	
<p>1. The following indications appeared on record concerning:</p> <p><input checked="" type="checkbox"/> the applicant <input type="checkbox"/> the inventor <input type="checkbox"/> the agent <input type="checkbox"/> the common representative</p>			
Name and Address NESTE OY Keilaniemi FIN-02150 Espoo Finland	State of Nationality		State of Residence
	FI		FI
	Telephone No.		
	Facsimile No.		
	Teleprinter No.		
<p>2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:</p> <p><input type="checkbox"/> the person <input checked="" type="checkbox"/> the name <input type="checkbox"/> the address <input type="checkbox"/> the nationality <input type="checkbox"/> the residence</p>			
Name and Address NESTE CHEMICALS OY Keilaniemi FIN-02150 Espoo Finland	State of Nationality		State of Residence
	FI		FI
	Telephone No.		
	Facsimile No.		
	Teleprinter No.		
<p>3. Further observations, if necessary:</p>			
<p>4. A copy of this notification has been sent to:</p> <p><input checked="" type="checkbox"/> the receiving Office <input type="checkbox"/> the designated Offices concerned <input type="checkbox"/> the International Searching Authority <input checked="" type="checkbox"/> the elected Offices concerned <input type="checkbox"/> the International Preliminary Examining Authority <input type="checkbox"/> other:</p>			
The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Eugénia Santos Telephone No.: (41-22) 338.83.38		

PENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

REC'D 12 AUG 1999

WIPO PCT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference NEST 74 PCT	FOR FURTHER ACTION		See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/FI98/00329	International filing date (day/month/year) 14.04.1998	Priority date (day/month/year) 11.04.1997	
International Patent Classification (IPC) or national classification and IPC6 C 10 M 105/42, C 09 K 5/04, C 07 C 69/67			
Applicant Neste Oy et al			

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets, including this cover sheet.

This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 2 sheets.

3. This report contains indications relating to the following items:

- I Basis of the report
- II Priority
- III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV Lack of unity of invention
- V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI Certain documents cited
- VII Certain defects in the international application
- VIII Certain observations on the international application

Date of submission of the demand 24.09.1998	Date of completion of this report 09.08.1999
Name and mailing address of the IPEA/SE Patent- och registreringsverket Box 5055 S-102 42 STOCKHOLM Facsimile No. 08-667 72 88	Authorized officer Eva Johansson/ELY Telephone No. 08-782 25 00

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/FI98/00329

L Basis of the report

1. This report has been drawn on the basis of (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

 the international application as originally filed. the description, pages 1-11, as originally filed,

pages _____, filed with the demand,

pages _____, filed with the letter of _____,

pages _____, filed with the letter of _____

 the claims, Nos. _____, as originally filed,

Nos. _____, as amended under Article 19,

Nos. _____, filed with the demand,

Nos. 1-15, filed with the letter of 15.06.1999,

Nos. _____, filed with the letter of _____

 the drawings, sheets/fig _____, as originally filed,

sheets/fig _____, filed with the demand

sheets/fig _____, filed with the letter of _____

sheets/fig _____, filed with the letter of _____

2. The amendments have resulted in the cancellation of:

 the description, pages _____ the claims, Nos. _____ the drawings, sheets/fig _____

3. This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the supplemental Box (Rule 70.2(c)).

4. Additional observations, if necessary:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/FI98/00329

V. Resoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	<u>3-4 and 13-14</u>	YES
	Claims	<u>1-2, 5-8, 9, 10-12, 15</u>	NO
Inventive step (IS)	Claims		YES
	Claims	<u>1-15</u>	NO
Industrial applicability (IA)	Claims	<u>1-15</u>	YES
	Claims		NO

2. Citations and explanations

This statement is based on the amended claims filed with the letter of 15 June 1999.

The claimed invention according to the amended claim 1 relates to a refrigerant composition comprising a chlorine-free hydrofluorocarbon refrigerant and, mixed therewith, a lubricant containing a polyol ester that comprises a mixture of an ester of 3-hydroxy-2, 2-dimethyl-propyl-3-hydroxy-2, 2-dimethylpropionate (HPHP) and an ester of another polyol. The invention also relates to a complex ester of 3-hydroxy-2, 2-dimethyl-propyl-3-hydroxy-2, 2-dimethylpropionate which contains residues of both mono- and dibasic carboxylic acids and the use of the complex ester in lubricants.

The following most relevant documents are cited in the search report:

- a) US 5374366 (in the first search report given as STN International, File CAPLUS, CAPLUS accession no. 1993:674910, Sanken Kako Kk: "Synthetic ester lubricating oils"; JP, A2, 05179267, 930720)
- b) STN International, File CAPLUS, CAPLUS accession no. 1995:951741, Sanken Kako Kk: "Compositions for refrigerator working fluids"; JP 07216372 A2
- c) File WPI, NIPPON OILS & FATS CO LTD: "Tert. fatty acid ester for lubricating oils - obtd. from tert. fatty acid and 2, 2,-di: methyl-3-hydroxypropyl 2, 2'-di: methyl-3'-hydroxy: propionate for good oxidn. stability; JP 4164046 A

.../...

Supplemental Box

(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: V.

a) relates to a synthetic lubricating oil, which is particularly miscible with hydrogen-containing fluoroalkane refrigerants, for example HFC-134, HFC-134a, HFC-143 or HFC-143a (see column 5, lines 24-32) and therefore can be used as a refrigerating machine oil (see column 1, lines 53-55). According to claim 14 in a) the lubricating oil comprises the esterification product of a hydroxycarboxylic acid polyol ester (A), at least one aliphatic monocarboxylic acid (B), an aliphatic carboxylic acid having two or more carboxyl groups (C) and an aliphatic polyhydric alcohol = polyol (D). A may be 3-hydroxy-2, 2-dimethyl-propyl-3-hydroxy-2, 2-dimethylpropionate = hydroxypivalic acid neopentyl glycol monoester = PHPH (see particularly claim 19). According to example 10 in a) PHPH (1 mole) is mixed and reacted with succinic acid (1 mole), neopentyl glycol (1 mole), 2-ethylhexanoic acid (1 mole) and caproic acid (1 mole) in the presence of a catalyst. Therefore, at least some part of the invention claimed in claim 1, namely when the polyol ester comprises a mixture of an ester of PHPH and a polyol ester of neopentylglycol, lacks novelty.

Several polyols (= polyhydric alcohols) are proposed in a) (see particularly claims 14-15 and 18-19). It is considered to be obvious for a person skilled in the art to use other polyols than neopentylglycol in the mixture. Therefore, the remaining part of claim 1 is not considered to involve an inventive step.

In view of example 10 in a) also the invention claimed in claims 2 and 5-8 lacks novelty. As mentioned above the known lubricating oil can be used with for example HFC-134, HFC-134a, HFC-143 or HFC-143a (see column 5, lines 24-32) and therefore can be used as a refrigerating machine oil (see column 1, lines 53-55). Therefore, also the invention claimed in claim 9 lacks novelty.

Furthermore, according to for example examples 6, 7 and 8 in a) PHPH is reacted with different amounts of 3,5,5-trimethylhexanoic acid and adipic acid, the molar ratio between the mono- and dibasic acids being within the claimed range according to claim 10 in the present application. Therefore, also the invention claimed in claims 10-12 and 15 lacks novelty.

.../...

Supplemental Box

(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: V.

The subject matter of the remaining claims, namely claims 3-4 and 13-14, has not been shown to involve anything but obvious matter to a person skilled in the art in view of the examples in a). Therefore, the invention claimed in claims 3-4 and 13-14 is not considered to involve an inventive step.

b) also relates to compositions for refrigerator working fluids consisting of ester compounds of hydroxycarboxylic acids polyol esters, aliphatic monocarboxylic acids, and optionally aliphatic polycarboxylic acids or aliphatic polycarboxylic acids and aliphatic polyvalent alcohols as refrigerator oils and hydrofluorocarbons as refrigerants. Preferably, the hydroxycarboxylic acid polyol esters are hydroxycarboxylic acid alkylene glycol esters (e.g., 3-hydroxy-2, 2-dimethylpropyl-3-hydroxy-2, 2-dimethylpropionic acid ester). b) is an abstract and thus not as detailed as a). It is considered to be of particular relevance as the exact ester and its use as a lubricant is given. Therefore, the claims are considered to lack the same requirements as in view of a).

c) (which is also an abstract) relates to tertiary fatty acid esters for lubricating oils, which are obtained from a mixture of tertiary fatty acids and dibasic acids (component 1) and 2, 2, -dimethyl-3-hydroxypropyl-2, 2-dimethyl-3-hydroxypropionate (component 2). The esters are appropriate as base oils for lubricating oils. However, c) does not relate to mixtures of esters of HPHP and other polyol esters. This document only discloses the general state of the art, which is not considered to be of particular relevance.

Claim 13 would be connected to any of claims 10 to 12 instead of any of claims 16 to 19.

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Claims:

1. Refrigerant composition comprising a chlorine-free hydrofluorocarbon based refrigerant and, mixed therewith, a lubricant containing a polyol ester, characterized in that the polyol ester comprises a mixture of an ester of 3-hydroxy-2,2-dimethyl-propyl-3-hydroxy-2,2-dimethylpropionate and
 - an ester of trimethylol propane, trimethylol ethane, pentaerythritol or 2,2,4-trimethylpentadiol, the amount of the 3-hydroxy-2,2-dimethyl-propyl-3-hydroxy-2,2-dimethylpropionate being at least 50 mol-% of the polyol residue of the ester mixture,
 - an ester of 2-butyl-2-ethyl-1,3-propanediol, the molar ratio of the 2-butyl-2-ethyl-1,3-propanediol and the 3-hydroxy-2,2-dimethyl-propyl-3-hydroxy-2,2-dimethylpropionate being 5:95 - 99:1, or
 - a polyol ester of neopentylglycol, 2-ethyl-1,3-hexanediol or 1,4-dimethylolcyclohexane.
2. The refrigerant composition according to claim 1, wherein the polyol ester mixture is prepared *in situ*.
3. The refrigerant composition according to claim 1 or claim 2, wherein the carboxylic acid residue of the polyol ester is derived from a linear or branched C₄...C₁₈-carboxylic acid, or an anhydrides thereof, or it is derived from a mixture of linear or branched C₄...C₁₈-carboxylic acids or anhydrides thereof.
4. The refrigerant composition according to claim 3, wherein the carboxylic acid residue is derived from 2-ethylhexanoic acid, heptanoic acid, octanoic acid and/or lauric acid.
5. The refrigerant composition according to claim 1, wherein the carboxylic acid residue of the ester is derived from a mixture of mono- and dibasic carboxylic acids.
6. The refrigerant composition according to claim 5, wherein the monobasic carboxylic acid residue is derived from linear or branched C₄...C₁₈-carboxylic acids or anhydrides or mixtures thereof.
7. The refrigerant composition according to claim 5 or claim 6, wherein the dibasic carboxylic acid residue is derived from oxalic acid, malonic acid, dimethylmalonic acid,

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succinic acid, glutaric acid, adipic acid, sebasic acid, pimelic acid, suberic acid or azelaic acid, or a cyclic anhydride such as succinic anhydride or an alkyl derivative thereof, or trimellitic anhydride.

- 5 8. The refrigerant composition according to any of claims 5 to 7, wherein the molar ratio between the mono- and dibasic carboxylic acids is 50:50 to 95:5.
- 10 9. The refrigerant composition according to any of the preceding claims, wherein the fluorinated hydrocarbon based refrigerant is hydrofluorocarbon 134, hydrofluorocarbon 134a, hydrofluorocarbon 143, hydrofluorocarbon 143a, hydrofluorocarbon 152 or hydrofluorocarbon 152a or a mixture of hydrofluorocarbons.
- 15 10. Complex esters of 3-hydroxy-2,2-dimethyl-propyl-3-hydroxy-2,2-dimethylpropionate which contain residues of both mono- and dibasic carboxylic acids, the molar ratio between the mono- and dibasic carboxylic acid residues in the ester being 50:50 to 95:5.
- 20 11. The complex esters according to claim 10, wherein the monobasic carboxylic acid residues are derived from linear or branched C₄...C₁₈-carboxylic acids or anhydrides or mixtures thereof.
- 25 12. The complex esters according to claim 10 or claim 11, wherein the dibasic carboxylic acid residues are derived from oxalic acid, malonic acid, dimethyl malonic acid, succinic acid, glutaric acid, adipic acid, sebasic acid, pimelic acid, suberic acid or azelaic acid, or a cyclic anhydride such as succinic anhydride or an alkyl derivative thereof, or trimellitic anhydride.
- 30 13. The complex esters according to any of claims 16 to 19, mixed with esters and/or complex esters of another polyol.
14. The complex esters according to claim 13, wherein the esters are in a mixture of esters and/or complex esters of NPG or BEPD.
15. The use of an ester according to any of claims 10 to 14 as base oils for lubricants.

replaced by Article 34
Claims:

1. Refrigerant composition comprising a chlorine-free hydrofluorocarbon based refrigerant and, mixed therewith, a lubricant containing a polyol ester, characterized in that the polyol ester comprises essentially totally an ester of 3-hydroxy-2,2-dimethyl-propyl-3-hydroxy-2,2-dimethylpropionate.

5 2. The refrigerant composition according to claim 1, wherein the polyol ester is to more than 95 mol-% constituted by an ester of 3-hydroxy-2,2-dimethylpropyl-3-hydroxy-2,2-dimethylpropionate.

10 3. Refrigerant composition comprising a chlorine-free hydrofluorocarbon based refrigerant and, mixed therewith, a lubricant containing a polyol ester, characterized in that the polyol ester comprises a mixture of an ester of 3-hydroxy-2,2-dimethyl-propyl-3-hydroxy-2,2-dimethylpropionate and an ester of trimethylol propane, trimethylol ethane, pentaerythritol or 2,2,4-trimethylpentadiol.

15 4. The refrigerant composition according to claim 3, wherein the molar ratio of the 3-hydroxy-2,2-dimethyl-propyl-3-hydroxy-2,2-dimethylpropionate is 50 to 100 %.

20 5. Refrigerant composition comprising a chlorine-free hydrofluorocarbon based refrigerant and, mixed therewith, a lubricant containing a polyol ester, characterized in that the polyol ester comprises a mixture of an ester of 3-hydroxy-2,2-dimethyl-propyl-3-hydroxy-2,2-dimethylpropionate and an ester of 2-butyl-2-ethyl-1,3-propanediol.

25 6. The refrigerant composition according to claim 5, wherein the molar ratio of the 2-butyl-2-ethyl-1,3-propanediol and the 3-hydroxy-2,2-dimethyl-propyl-3-hydroxy-2,2-dimethylpropionate is 5:95 - 99:1.

30 7. Refrigerant composition comprising a chlorine-free hydrofluorocarbon based refrigerant and, mixed therewith, a lubricant containing a polyol ester, characterized in that the polyol ester comprises a mixture of an ester of 3-hydroxy-2,2-dimethyl-propyl-3-hydroxy-2,2-dimethylpropionate and a polyol ester of neopentylglycol, 2-ethyl-1,3-hexanediol or 1,4-dimethylol-cyclohexane.

35 8. The refrigerant composition according to any of claims 3 to 7, wherein the polyol ester

mixture is prepared *in situ*.

9. The refrigerant composition according to any of the preceding claims, wherein the carboxylic acid residue of the polyol ester is derived from a linear or branched C₄...C₁₈-carboxylic acid, or an anhydrides thereof, or it is derived from a mixture of linear or branched C₄...C₁₈-carboxylic acids or anhydrides thereof.

10. The refrigerant composition according to claim 9, wherein the carboxylic acid residue is derived from 2-ethylhexanoic acid, heptanoic acid, octanoic acid and/or lauric acid.

11. The refrigerant composition according to claim 1, wherein the carboxylic acid residue of the ester is derived from a mixture of mono- and dibasic carboxylic acids.

12. The refrigerant composition according to claim 11, wherein the monobasic carboxylic acid residue is derived from linear or branched C₄...C₁₈-carboxylic acids or anhydrides or mixtures thereof.

13. The refrigerant composition according to claim 11 or claim 12, wherein the dibasic carboxylic acid residue is derived from oxalic acid, malonic acid, dimethylmalonic acid, succinic acid, glutaric acid, adipic acid, sebasic acid, pimelic acid, suberic acid or azelaic acid, or a cyclic anhydride such as succinic anhydride or an alkyl derivative thereof, or trimellitic anhydride.

14. The refrigerant composition according to any of claims 11 to 13, wherein the molar ratio between the mono- and dibasic carboxylic acids is 50:50 to 95:5.

15. The refrigerant composition according to any of the preceding claims, wherein the fluorinated hydrocarbon based refrigerant is hydrofluorocarbon 134, hydrofluorocarbon 134a, hydrofluorocarbon 143, hydrofluorocarbon 143a, hydrofluorocarbon 152 or hydrofluorocarbon 152a or a mixture of hydrofluorocarbons.

16. Complex esters of 3-hydroxy-2,2-dimethyl-propyl-3-hydroxy-2,2-dimethylpropionate which contain residues of both mono- and dibasic carboxylic acids.

17. The complex esters according to claim 16, wherein the monobasic carboxylic acid residues are derived from linear or branched C₄...C₁₈-carboxylic acids or anhydrides or

mixtures thereof.

18. The complex esters according to claim 16 or claim 17, wherein the dibasic carboxylic acid residues are derived from oxalic acid, malonic acid, dimethyl malonic acid, succinic acid, glutaric acid, adipic acid, sebasic acid, pimelic acid, suberic acid or azelaic acid, or a cyclic anhydride such as succinic anhydride or an alkyl derivative thereof, or trimellitic anhydride.
19. The complex esters according to any of claims 16 to 18, wherein the molar ratio between the mono- and dibasic carboxylic acid residues in the ester is 50:50 to 95:5.
20. The complex esters according to any of claims 16 to 19, which are mixed with esters and/or complex esters of another polyol.
- 15 21. The complex esters according to claim 20, wherein the esters are in a mixture of esters and/or complex esters of NPG or BEPD.
22. The use of an ester according to any of claims 16 to 21 as base oils for lubricants.

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REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference
(if desired) (12 characters maximum) NEST 74 PCT

Box No. I TITLE OF INVENTION Polyol and complex esters for use with, in particular, fluorinated refrigerants

Box No. II APPLICANT

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (i.e. country) of residence if no State of residence is indicated below.)

NESTE OY
Keilaniemi
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Finland

This person is also inventor.

Telephone No.

Faximile No.

Teleprinter No.

State (i.e. country) of nationality:
Finland

State (i.e. country) of residence:
Finland

This person is applicant all designated States all designated States except the United States of America the United States of America only the States indicated in the Supplemental Box for the purposes of:

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (i.e. country) of residence if no State of residence is indicated below.)

KOISTINEN, Jari
Lamminmutka 2 C 14
FIN-40520 Jyväskylä
Finland

This person is:

applicant only

applicant and inventor

inventor only (If this check-box is marked, do not fill in below.)

State (i.e. country) of nationality:
Finland

State (i.e. country) of residence:
Finland

This person is applicant all designated States all designated States except the United States of America the United States of America only the States indicated in the Supplemental Box for the purposes of:

Further applicants and/or (further) inventors are indicated on a continuation sheet.

Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:

agent common representative

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

of LAINE, Seppo; SUNDMAN, Christoffer;
LIPSANEN, Jari; HOVI, Simo; and
KNUTH-LEPTOLA, Sisko
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Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Continuation of Box No. III FURTHER APPLICANTS AND/OR (FURTHER) INVENTORS

If none of the following sub-boxes is used, this sheet is not to be included in the request.

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (i.e. country) of residence if no State of residence is indicated below.)

RISSANEN, Kari
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FIN-41520 Hankasalmi
Finland

This person is:

- applicant only
 applicant and inventor
 inventor only (If this check-box is marked, do not fill in below.)

State (i.e. country) of nationality:
FinlandState (i.e. country) of residence:
Finland

This person is applicant all designated States all designated States except the United States of America the United States of America only the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (i.e. country) of residence if no State of residence is indicated below.)

SILVENNOINEN, Laura
Kilpisenkatu 16 A 20
FIN-40100 Jyväskylä
Finland

This person is:

- applicant only
 applicant and inventor
 inventor only (If this check-box is marked, do not fill in below.)

State (i.e. country) of nationality:
FinlandState (i.e. country) of residence:
Finland

This person is applicant all designated States all designated States except the United States of America the United States of America only the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (i.e. country) of residence if no State of residence is indicated below.)

KOSKIMIES, Salme
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Finland

This person is:

- applicant only
 applicant and inventor
 inventor only (If this check-box is marked, do not fill in below.)

State (i.e. country) of nationality:
FinlandState (i.e. country) of residence:
Finland

This person is applicant all designated States all designated States except the United States of America the United States of America only the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (i.e. country) of residence if no State of residence is indicated below.)

This person is:

- applicant only
 applicant and inventor
 inventor only (If this check-box is marked, do not fill in below.)

State (i.e. country) of nationality:

State (i.e. country) of residence:

This person is applicant all designated States all designated States except the United States of America the United States of America only the States indicated in the Supplemental Box

Further applicants and/or (further) inventors are indicated on another continuation sheet.

Box N .V DESIGNATION OF STATES

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes; at least one must be marked):

Regional Patent

- AP ARIPO Patent: GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SZ Swaziland, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- EA Eurasian Patent: AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- EP European Patent: AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- OA OAPI Patent: BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)

National Patent (if other kind of protection or treatment desired, specify on dotted line):

- | | |
|--|--|
| <input checked="" type="checkbox"/> AL Albania | <input checked="" type="checkbox"/> LT Lithuania |
| <input checked="" type="checkbox"/> AM Armenia | <input checked="" type="checkbox"/> LU Luxembourg |
| <input checked="" type="checkbox"/> AT Austria | <input checked="" type="checkbox"/> LV Latvia |
| <input checked="" type="checkbox"/> AU Australia | <input checked="" type="checkbox"/> MD Republic of Moldova |
| <input checked="" type="checkbox"/> AZ Azerbaijan | <input checked="" type="checkbox"/> MG Madagascar |
| <input checked="" type="checkbox"/> BA Bosnia and Herzegovina | <input checked="" type="checkbox"/> MK The former Yugoslav Republic of Macedonia |
| <input checked="" type="checkbox"/> BB Barbados | <input checked="" type="checkbox"/> |
| <input checked="" type="checkbox"/> BG Bulgaria | <input checked="" type="checkbox"/> MN Mongolia |
| <input checked="" type="checkbox"/> BR Brazil | <input checked="" type="checkbox"/> MW Malawi |
| <input checked="" type="checkbox"/> BY Belarus | <input checked="" type="checkbox"/> MX Mexico |
| <input checked="" type="checkbox"/> CA Canada | <input checked="" type="checkbox"/> NO Norway |
| <input checked="" type="checkbox"/> CH and LI Switzerland and Liechtenstein | <input checked="" type="checkbox"/> NZ New Zealand |
| <input checked="" type="checkbox"/> CN China | <input checked="" type="checkbox"/> PL Poland |
| <input checked="" type="checkbox"/> CU Cuba | <input checked="" type="checkbox"/> PT Portugal |
| <input checked="" type="checkbox"/> CZ Czech Republic | <input checked="" type="checkbox"/> RO Romania |
| <input checked="" type="checkbox"/> DE Germany | <input checked="" type="checkbox"/> RU Russian Federation |
| <input checked="" type="checkbox"/> DK Denmark | <input checked="" type="checkbox"/> SD Sudan |
| <input checked="" type="checkbox"/> EE Estonia | <input checked="" type="checkbox"/> SE Sweden |
| <input checked="" type="checkbox"/> ES Spain | <input checked="" type="checkbox"/> SG Singapore |
| <input checked="" type="checkbox"/> FI Finland | <input checked="" type="checkbox"/> SI Slovenia |
| <input checked="" type="checkbox"/> GB United Kingdom | <input checked="" type="checkbox"/> SK Slovakia |
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| <input checked="" type="checkbox"/> GW Guinea-Bissau | <input checked="" type="checkbox"/> TR Turkey |
| <input checked="" type="checkbox"/> HU Hungary | <input checked="" type="checkbox"/> TT Trinidad and Tobago |
| <input checked="" type="checkbox"/> ID Indonesia | <input checked="" type="checkbox"/> UA Ukraine |
| <input checked="" type="checkbox"/> IL Israel | <input checked="" type="checkbox"/> UG Uganda |
| <input checked="" type="checkbox"/> IS Iceland | <input checked="" type="checkbox"/> US United States of America |
| <input checked="" type="checkbox"/> JP Japan | <input checked="" type="checkbox"/> |
| <input checked="" type="checkbox"/> KE Kenya | <input checked="" type="checkbox"/> UZ Uzbekistan |
| <input checked="" type="checkbox"/> KG Kyrgyzstan | <input checked="" type="checkbox"/> VN Viet Nam |
| <input checked="" type="checkbox"/> KP Democratic People's Republic of Korea | <input checked="" type="checkbox"/> YU Yugoslavia |
| <input checked="" type="checkbox"/> KR Republic of Korea | <input checked="" type="checkbox"/> ZW Zimbabwe |
| <input checked="" type="checkbox"/> KZ Kazakhstan | <input type="checkbox"/> |
| <input checked="" type="checkbox"/> LC Saint Lucia | <input type="checkbox"/> |
| <input checked="" type="checkbox"/> LK Sri Lanka | <input type="checkbox"/> |
| <input checked="" type="checkbox"/> LR Liberia | <input type="checkbox"/> |
| <input checked="" type="checkbox"/> LS Lesotho | <input type="checkbox"/> |

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In addition to the designations made above, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except the designation(s) of _____.

The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation of a designation consists of the filing of a notice specifying that designation and the payment of the designation and confirmation fees. Confirmation must reach the receiving Office within the 15-month time limit.)

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Box N . VI PRIORITY CLAIMFurther priority claims are indicated in the Supplemental Box

The priority of the following earlier application(s) is hereby claimed:

Country (in which, or for which, the application was filed)	Filing Date (day/month/year)	Application No.	Office of filing (only for regional or international application)
item (1) Finland	11 April 1997	971548	
item (2) Finland	11 April 1997	971549	
item (3) Finland	31 March 1998	980730	

Mark the following check-box if the certified copy of the earlier application is to be issued by the Office which for the purposes of the present international application is the receiving Office (a fee may be required):

The receiving Office is hereby requested to prepare and transmit to the International (1, 2, 3)
Bureau a certified copy of the earlier application(s) identified above as item(s):

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) (If two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used): ISA / SE

Earlier search Fill in where a search (international, international-type or other) by the International Searching Authority has already been carried out or requested and the Authority is now requested to base the international search, to the extent possible, on the results of that earlier search. Identify such search or request either by reference to the relevant application (or the translation thereof) or by reference to the search request:

Country (or regional Office): Date (day/month/year): Number:

Box No. VIII CHECK LIST

This international application contains the following number of sheets:	This international application is accompanied by the item(s) marked below:	
1. request : 4 sheets	1. <input type="checkbox"/> separate signed power of attorney	5. <input checked="" type="checkbox"/> fee calculation sheet
2. description : 11 sheets	2. <input type="checkbox"/> copy of general power of attorney	6. <input type="checkbox"/> separate indications concerning deposited microorganisms
3. claims : 3 sheets	3. <input type="checkbox"/> statement explaining lack of signature	7. <input type="checkbox"/> nucleotide and/or amino acid sequence listing (diskette)
4. abstract : 1 sheets	4. <input type="checkbox"/> priority document(s) identified in Box No. VI as item(s):	8. <input checked="" type="checkbox"/> other (specify): copies of official actions
5. drawings : - sheets		
Total : 19 sheets		

Figure No. _____ of the drawings (if any) should accompany the abstract when it is published.

Box No. IX SIGNATURE OF APPLICANT OR AGENT

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

Seppo Laine Oy

For the Applicants

Christoffer Sundman

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1. Date of actual receipt of the purported international application:	2. Drawings: <input type="checkbox"/> received: <input type="checkbox"/> not received:
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:	
4. Date of timely receipt of the required corrections under PCT Article 11(2):	
5. International Searching Authority specified by the applicant: ISA /	6. <input type="checkbox"/> Transmittal of search copy delayed until search fee is paid

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REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

International Application No. PCT/FI 98 / 00329

International Filing Date 14 APR 1998 (14.04.98)

The Finnish Patent Office
PCT International Application

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference
(if desired) (12 characters maximum) NEST 74 PCT

B x No. I TITLE OF INVENTION

Polyol and complex esters for use with, in particular, fluorinated refrigerants

Box No. II APPLICANT

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (i.e. country) of residence if no State of residence is indicated below.)

NESTE OY
Keilaniemi
FIN-02150 Espoo
Finland

This person is also inventor.

Telephone No.

Faximile No.

Teleprinter No.

State (i.e. country) of nationality:
Finland

State (i.e. country) of residence:
Finland

This person is applicant all designated States all designated States except the United States of America the United States of America only the States indicated in the Supplemental Box for the purposes of:

B x No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (i.e. country) of residence if no State of residence is indicated below.)

KOISTINEN, Jari
Lamminmäki 2 C 14
FIN-40520 Jyväskylä
Finland

This person is:

applicant only

applicant and inventor

inventor only (If this check-box is marked, do not fill in below.)

State (i.e. country) of nationality:
Finland

State (i.e. country) of residence:
Finland

This person is applicant all designated States all designated States except the United States of America the United States of America only the States indicated in the Supplemental Box for the purposes of:

Further applicants and/or (further) inventors are indicated on a continuation sheet.

B x No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:

agent

common representative

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

of LAINE, Seppo; SUNDMAN, Christoffer;
LIPSANEN, Jari; HOVI, Simo; and
KNUTH-LEHTOLA, Sisko
SEPRO LAINE OY
Lönnrotinkatu 19 A
FIN-00120 Helsinki, Finland

Telephone No.

+358-9-69 32 600

Faximile No.

+358-9-69 32 910

Teleprinter No.

Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Continuation f Box No. III FURTHER APPLICANTS AND/OR (FURTHER) INVENTORS

If none of the following sub-boxes is used, this sheet is not to be included in the request.

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (i.e. country) of residence if no State of residence is indicated below.)

RISSANEN, Kari
Hankamäentie 13
FIN-41520 Hankasalmi
Finland

This person is:

- applicant only
 applicant and inventor
 inventor only (If this check-box is marked, do not fill in below.)

State (i.e. country) of nationality:
FinlandState (i.e. country) of residence:
Finland

This person is applicant for the purposes of: all designated States all designated States except the United States of America the United States of America only the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (i.e. country) of residence if no State of residence is indicated below.)

SILVENNOINEN, Laura
Kilpisenkatu 16 A 20
FIN-40100 Jyväskylä
Finland

This person is:

- applicant only
 applicant and inventor
 inventor only (If this check-box is marked, do not fill in below.)

State (i.e. country) of nationality:
FinlandState (i.e. country) of residence:
Finland

This person is applicant for the purposes of: all designated States all designated States except the United States of America the United States of America only the States indicated in the Supplemental Box

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KOSKIMIES, Salme
Hämeenpajantie 7
FIN-00850 Helsinki
Finland

This person is:

- applicant only
 applicant and inventor
 inventor only (If this check-box is marked, do not fill in below.)

State (i.e. country) of nationality:
FinlandState (i.e. country) of residence:
Finland

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- applicant only
 applicant and inventor
 inventor only (If this check-box is marked, do not fill in below.)

State (i.e. country) of nationality:

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This person is applicant for the purposes of: all designated States all designated States except the United States of America the United States of America only the States indicated in the Supplemental Box

Further applicants and/or (further) inventors are indicated on another continuation sheet.

B x No.V DESIGNATION OF STATES

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes; at least one must be marked):

Regional Patent

- AP ARIPO Patent: GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SZ Swaziland, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- EA Eurasian Patent: AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- EP European Patent: AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- OA OAPI Patent: BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)

National Patent (if other kind of protection or treatment desired, specify on dotted line):

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|--|--|
| <input checked="" type="checkbox"/> AL Albania | <input checked="" type="checkbox"/> LT Lithuania |
| <input checked="" type="checkbox"/> AM Armenia | <input checked="" type="checkbox"/> LU Luxembourg |
| <input checked="" type="checkbox"/> AT Austria | <input checked="" type="checkbox"/> LV Latvia |
| <input checked="" type="checkbox"/> AU Australia | <input checked="" type="checkbox"/> MD Republic of Moldova |
| <input checked="" type="checkbox"/> AZ Azerbaijan | <input checked="" type="checkbox"/> MG Madagascar |
| <input checked="" type="checkbox"/> BA Bosnia and Herzegovina | <input checked="" type="checkbox"/> MK The former Yugoslav Republic of Macedonia |
| <input checked="" type="checkbox"/> BB Barbados | <input checked="" type="checkbox"/> MN Mongolia |
| <input checked="" type="checkbox"/> BG Bulgaria | <input checked="" type="checkbox"/> MW Malawi |
| <input checked="" type="checkbox"/> BR Brazil | <input checked="" type="checkbox"/> MX Mexico |
| <input checked="" type="checkbox"/> BY Belarus | <input checked="" type="checkbox"/> NO Norway |
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Box No. VI PRIORITY CLAIMFurther priority claims are indicated in the Supplemental Box

The priority of the following earlier application(s) is hereby claimed:

Country (in which, or for which, the application was filed)	Filing Date (day/month/year)	Application No.	Office of filing (only for regional or international application)
item (1) Finland	(11.04.97) 11 April 1997	971548	
item (2) Finland	(11.04.97) 11 April 1997	971549	
item (3) Finland	(31.03.98) 31 March 1998	980730	

Mark the following check-box if the certified copy of the earlier application is to be issued by the Office which for the purposes of the present international application is the receiving Office (a fee may be required):

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Box No. VII INTERNATIONAL SEARCHING AUTHORITY

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1. request : 4 sheets	1. <input type="checkbox"/> separate signed power of attorney	5. <input checked="" type="checkbox"/> fee calculation sheet
2. description : 11 sheets	2. <input type="checkbox"/> copy of general power of attorney	6. <input type="checkbox"/> separate indications concerning deposited microorganisms
3. claims : 3 sheets	3. <input type="checkbox"/> statement explaining lack of signature	7. <input type="checkbox"/> nucleotide and/or amino acid sequence listing (diskette)
4. abstract : 1 sheets	4. <input type="checkbox"/> priority document(s) identified in Box No. VI as item(s):	8. <input checked="" type="checkbox"/> other (specify): copies of official actions
5. drawings : - sheets		
Total : 19 sheets		

Figure No. _____ of the drawings (if any) should accompany the abstract when it is published.

Box No. IX SIGNATURE OF APPLICANT OR AGENT

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

Seppo Laine Oy

For the Applicants



Christoffer Sundman

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1. Date of actual receipt of the purported international application:	14 APR 1998	(14-04-1998)
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2. Drawings:		
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Etenkin fluorattujen jäähdytysnesteiden kanssa käytettäväät polyoli- ja kompleksiesterit

- 5 Esillä oleva keksintö koskee patenttivaatimusten 1, 3, 5 ja 7 johdantojen mukaisia jäähdytysnestekostumusta. Tällaiset koostumukset sisältävät yleensä kloorittoman fluorihiilivetypohjaisen jäähdytysaineen sekä siihen sekoittuneen, polyoliesteriä sisältävän voiteluaineen.
- 10 Keksintö koskee myös patenttivaatimuksen 16 mukaisia kompleksiesteriteitä sekä näiden käyttöä voiteluaineissa.

Polyoliesterityyppisten voiteluaineiden kehitys on viime aikoina ollut nopeaa, mikä johtuu useilla sovellusalueilla tapahtuvasta kehityksestä. Näitä tuotteita voidaan käyttää sellaisenaan perusvoiteluaineena esimerkiksi lentokone- ja kaasuturbiinimoottoreissa tai seoksena hiilivetypohjaisten voiteluaineiden kanssa, biohajoavina hydrauliöljyinä, kompressorioiljyinä, metallien työstö-öljyinä sekä erityisesti fluorattujen jäähdytysnesteiden kanssa liuokoisena voiteluainekomponenttina jäähdytyskompressoreissa niiden suotuisien liuokoisuus ominaisuuksien ja hyvän teknisen stabiilisuuden johdosta.

- 20 Jäähdytysnesteiden kanssa on ehdotettu käytettäväksi yleisesti mm. neopentyyliglykolin ja pentaerytritolin estereitä. Vaikka näillä tunnetuilla estereillä on periaatteessa hyvät voiteluaine ominaisuudet, niiden liuokoisuus kloorittomaan fluorihiilivetyihin on useimmiten vain tyydyttävä. Tästä syystä ne kaikki eivät toimi riittävän hyvin juuri fluorattujen hiilivetyjä sisältävissä jäähdytysnestekostumuksista.

- 25 Esillä olevan keksinnön tarkoituksena on poistaa tunnettuihin ratkaisuihin liittyvät epäkohdat ja saada aikaan uudenlaisia polyoli- ja kompleksiesteriteitä, joita voidaan käyttää etenkin fluorattujen jäähdytysnesteiden kanssa voiteluaineina. Keksinnön tarkoituksena on edelleen saada aikaan uudenlaisia estereitä, jotka soveltuват yleisesti voiteluaineiden perusöljyiksi.

- 30 Keksintö perustuu siihen havaintoon, että 3-hydroksi-2,2-dimetyylipropyyli-3-hydroksi-2,2-dimetyylipropionaatti eli hydroksipivalyylihydroksipivalaatin polyoli- tai kompleksiesterit, joilla on hyvät voiteluaineominaisuudet, liukenevat myös hyvin tai erittäin hyvin fluorattuihin jäähdytysnesteisiin ja ne soveltuvat siksi käytettäviksi tällaisia jäähdytysnes-

teitä sisältävissä jäähytysaineeseoksissa. Etenkin voiteluaineina käytetään polyoliesterit, joissa polyoli on HPHP (hydroksipivalyylihydroksipivalatti) joko sellaisenaan tai yhdessä toisen polyolin, kuten NPG:n, BEPD:n, ETHD:n, TMP:n, TME:n tai PE:n kanssa ja karboksylihappo on C₅ - C₁₈ lineaarinen tai haaroittunut monokarboksylihappo tai hydroksihappo, kuten hydroksipivaliinihappo tai mono- ja dikarboksylihappojen, kuten adipiinihapon, sebasiinihapon, atselaiinihapon, dimetyylimalonihapon tai syklisten anhydridien seos.

Täsmällisemmin sanottuna keksinnön mukaiselle jäähytysaineekostumukselle on pääasiallisesti tunnusomaista se, mikä on esitetty patenttivaatimusten 1, 3, 5 ja 7 tunnusmerkkiosissa.

HPHP:n kompleksiesterit ovat uusia ja käyttökelpoisia voiteluöljyjen perusöljyjä. Uusille estereille on tunnusomaista se, mikä on esitetty patenttivaatimuksen 16 tunnusmerkkiossa.

Keksinnön avulla saavutetaan huomattavia etuja. Niinpä, kuten edellä todettiin, HPHP:n estereillä on hyvät voiteluaineominaisuudet sekä hyvä liukoisuus jäähytysnesteenä käytettyihin HFC-yhdisteisiin. Öljyjen perusraaka-aineet voidaan tuottaa taloudellisesti edullisella okso-prosessilla (hydroformulointi). Öljyjen ominaisuuksia voidaan helposti modifioida käyttökohteen mukaan vaihtelemalla joko esterien polyolien suhdetta (HPHP:n määrä voi olla 100 - 5 mol-% polyolin kokonaismäärästä), esteröitäävää karboksylihappoa ja/tai esteröivien karboksylihappojen keskinäistä suhdetta. Käyttämällä haaroittuneita hiilivetyjä voidaan liuokoisuutta parantaa ja käyttämällä kaksiarvoisia happoja voidaan viskositeettia nostaa.

Keksintöä ryhdytään seuraavassa lähemmin tarkastelemaan yksityiskohtaisen selostuksen ja muutaman sovellusesimerkin avulla.

Esillä olevat esterit käsittevät 3-hydroksi-2,2-dimetylipropyli-3-hydroksi-2,2-dimetylipropionaatin polyoli- ja kompleksiesterit. "Polyoliesterellä" tarkoitetaan tällöin mm. estereitä, joiden karboksylyryhmä on yksiarvoinen happo tai tämän anhydridi. Tässä keksinnössä "polyoliesteri" -käsite kattaa yleisessä muodossaan myös "kompleksiesterit", jotka ovat estereitä, joissa ainakin osa esteröivistä karboksylihappoista on kaksiarvoisia. Tavallisesti näiden happojen molemmat karboksylyryhmät reagoivat alkoholien kanssa, jolloin saadaan oligomeerisiä esteriyhdisteitä, jotka sisältävät kaksi alkoholitähdettä ja .

yhden karboksyylihappotähteen. Kompleksiesteriin luetaan myös ne esterit, joiden karboksyylihappotähteen muodostaa hydroksihapot, joissa on läsnä sekä hydroksyyliryhmä että karboksyili-happoryhmä. Karboksyyliryhmä reagoi tällöin esim. polyolin kanssa ja hydroksyyliryhmä toisen karboksyylipon karboksyyliryhmän kanssa.

5

“Polyoli” tarkoittaa yhdistettä, jossa on ainakin kaksi hydroksyyliryhmää. Keksinnön mukaan HPHP voidaan esteröidä sellaisenaan (eli voidaan tuottaa polyoliesteri yhdessä jonkin toisen polyolin kanssa, joista esimerkkinä voidaan mainita NPG (neopentyliglykoli), BEPD (2-butylyli-2-etyyli-1,3-propaani-dioli), ETHD (2-etyyli-1,3-heksaanidioli), 10 TMP (trimetylolpropaani), TME (trimetyloli-etaani), PE (pentaerytritoli), TMPD (2,2,4-trimetylpentadioli) ja CHDM (1,4-dimetyloli-sykloheksaani). Näistä polyoleista kemiallisesti ja teknisesti stabiilit polyolit, joiden 2-hiilessä ei ole vetyä tai jotka ovat (steerisesti) vahvasti estyneitä, kuten NPG, ETHD, CHDM ja BEPD, ovat erityisen edullisia.

10

15 Edullisesti polyoliesterien seokset muodostetaan sekoittamalla polyolit keskenään ja esteröimällä näin saatu seos *in situ*.

Keksinnön ensimmäisen edullisen sovellusmuodon mukaan saadaan aikaan jäähdyytysaineeseos, joka sisältää polyoliesteriä, joka kokonaan tai lähes kokonaan (yli 95 mooli-%, 20 jopa 100 %) koostuu HPHP:n esteristä.

Keksinnön toisen edullisen sovellusmuodon mukaan saadaan aikaan jäähdyytysaineeseos, joka sisältää HPHP:n polyoliesterin lisäksi ainakin TMP:n, TME:n, PE:n tai TMPD:n esterin missä vain halutussa suhteessa. Edullisesti HPHP muodostaa kuitenkin esteriseoksen polyolitähteen pääosan, eli sen mooliosuus on 50 % - 100 %.

Keksinnön kolmannen edullisen sovellusmuodon mukaan saadaan aikaan jäähdyytysaineeseos, joka sisältää HPHP:n polyoliesteri lisäksi BEPD:n polyoliesterin, jolloin BEPD:n ja HPHP:n moolisuhde on 5:95 - 99:1.

25

30 Keksinnön neljännen edullisen sovellusmuodon mukaan saadaan aikaan jäähdyytysaineeseos, joka sisältää HPHP:n polyoliesteri lisäksi NPG:n, ETHD:n tai CHDM:n polyoliesterin. ja BEPD, ovat erityisen edullisia.

35

HPHP tai HPHP:n ja jonkin toisen polyolin seos esteröidään lineaarisella tai haaroittuneella C_4-C_{18} karboksyylipolla tai tämän anhydridillä. Esimerkkinä alifaattisista, lineaaris-

ta tai haaroittuneista, tyydytetyistä tai tyydyttämättömistä C₄-C₁₈-karboksylihapoista, joita voidaan käyttää HPHP:n esterien valmistukseen voidaan mainita seuraavat:

- I tyydytetyt, lineaariset C₄-C₁₈-karboksylihapot, butaanihappo (voihappo), pentaanihappo (valeriaanahappo), heksaanihappo (kapronihappo), heptaanihappo, oktaanihappo (kapryylihappo), nonaanihappo (pelargonihappo), dekaanihappo (kapriinihappo), dodekaanihappo (lauriinihappo) ja heksadekaanihappo (palmitiinihappo) sekä näiden seokset,
- II tyydytetyt, haaroittuneet C₄-C₁₆-karboksylihapot: 2-etyyliheksaanihappo, isononaanihappo ja 3,5,5-trimetyyliheksaanihappo;
- III tyydyttämättömät, lineaariset C₄-C₁₈-karboksylihapot: 3-buteenihappo (vinyylietikkahappo);
- IV tyydyttämättömät, haaroittuneet C₄-C₁₈-karboksylihapot.

Sekaestereissä eri lineaaristen ja haaroittuneiden karboksylihappojen suhteet voivat vaihdella laajalla alueella. Tyypillisesti lineaarista (lineaarisia) karboksylihappoja on 1-100 mol-% karboksylihappojen määrästä, edullisesti noin 10 - 90 mol-%. Haaroittumeita karboksylihappoja on vastaavasti 99 - 1 mol-%, edullisesti noin 90 - 10 mol-%. Etenkin on mahdollista valmistaa polyoliestereitä, jotka sisältävät 10 - 50 mol-% ainakin yhtä lineaarista karboksylihappoa ja 90 - 50 mol-% haaroittunutta karboksylihappoa.

Valmistettaessa HPHP:n polyoliestereitä valitaan sopivimman esteröiviksi karboksylihappoiksi 4 - 14 hiiliatomia sisältävät lineaariset tai haaroittuneet hapot, joista esimerkkinä voidaan mainita pentaani-, heksaani-, heptaani-, oktaani-, 2-etyyliheksaani- ja lauriinihappo.

Esteröivistä hydroksihapoista voidaan mainita seuraavat: hydroksipivaalihappo (HPAA), maitohappo, sitruunahappo ja dimetylolipropionihappo (DMPA).

Edellisten lisäksi esteröivänä karboksylihappona voidaan käyttää kaksiemäksistä karboksylihappoa, kuten oksaalihappo, malonihappo, dimetyylimalonihappo, meripihkahappo, glutaarihappo, adipiinihappo, sebasiinihappo, pimeliinihappo, suberiinihappo tai atselaiinihappo. Voidaan myös käyttää syklistä anhydridiä, kuten meripihkahappoanhydridiä tai sen alkyylijohdannaisesta, tai trimellitiinianhydridistä. Myös aromaattiset anhydridit, kuten ftaalihappoanhydridi, ovat pienissä määrissä mahdollisia.

Polyolien esteröintiaste on 50 - 100 %, edullisesti mahdollisimman korkea, ainakin noin 90 %. Kompleksiestereissä yksi- ja kaksiemäksisten karboksylylihappojen suhde on 50:50 - 95:5.

- 5 HPHP:n tai HPHP:n ja ainakin yhden toisen polyolin estereistä/sekaestereistä/kompleksiestereistä voidaan valmistaa jäähdytysnestekootumuksia. Nämä sisältävät jäähdytysaineena kloorittoman fluorihilivedyn. Esimerkkinä koostumusten hiilivetykomponentista mainittakoon seuraavat: fluorihilivety 134 (1,1,2,2-tetrafluorietaani), fluorihilivety 134a, fluorihilivety 143 (1,1,2-trifluorietaani), fluorihilivety 143 a (1, 1, 1 -trifluorietaani), fluorihilivety 152 (1,2-difluorietaani) tai fluorihilivety 152a (1,1-difluorietaani). Näistä yhdisteistä fluorihilivetyä 134a pidetään yleensä edullisena. Fluorihilivetyjen seoksia voidaan myös käyttää. Näistä esimerkkinä mainittakoon fluorihilivetyseos 407 (hiilivetyjen 32, 125 ja 134a seos) ja fluorihilivetyseos 410 (hiilivetyjen 32 ja 125 seos).
- 10 15 Käyttökohteeseen mukaan esteriltä vaaditaan ISO-standardin mukainen viskositeetti vaihtelee välillä 5 ja 200 cSt (40 °C). Alhaisia (5 - 10) ja keskisuuria (22 - 32) viskositeettejä tarvitaan esim. jäakaapeissa ja muissa pienehköissä jäähdytyslaitteissa. Korkean viskositeetin (46 - 68) sovelluksia tarvitaan esim. ilmastoinnin jäähdytyslaitteissa.
- 20 25 30 Kuten alussa jo todettiin, voidaan valmistettavien estereiden viskositeetti saada halutuksi valitsemalla sopivasti esteröivät karboksylylihappokomponentit ja/tai lisäämällä jotaan toista polyolia HPHP:n sekä. Niinpä tavanomaisilla lineaarisilla ja haaroittuneilla karboksylylihapoilla (C_8-C_{12}) saadaan estereitä, joiden viskositeetit ovat noin 15 - 22 cSt 40 °C:ssa. Viskositteetindeksit ovat noin 100 ja jähmepisteet alle -40 °C. Lisäämällä haaroittuneen karboksylyhapon osuutta saadaan esterien liukoisuus kasvamaan. Tuomalla esteröintiin kaksiarvoisen karboksylyhappo ja etenkin käyttämällä sitä yhdessä lineaaristen ja haaroittuneiden happojen kanssa saadaan tuotteen viskositeetti kasvamaan. Kylmäominaisuudet ja hyvä liukoisuus säilyvät. Sekoittamalla HPHP jonkin toisen polyolin kanssa ennen esteröintiä voidaan esterin viskositeettiä vielä entisestä kasvattaa ilman, että liukoisuus huononee. Viskositteti nousee tällöin jopa korkean viskositeetin alueelle.

Esimerkkinä erityisen edullisista estereistä voidaan mainita seuraavat:

- I HPHP:n polyoliesterit, jotka sisältävät 30-60 mol-%:a lineaarista karboksylylihappoa ja 70-40 mol-%:a haaroittunutta karboksylyhappoa;
- II HPHP:n kompleksiesterit, jotka siältävät 1-10 mol-%:a kaksiemäksistä karbok-

syylihappoa ja 90-99 mol-%:a lineaarista ja/tai haaroittunutta yksiarvoista karboksylihappoa; sekä.

III HPHP:n ja NPG:n/BEPD:n kompleksiesterit, jotka sisältävät 4-30 mol-%:a kaksi-emäksistä karboksylihappoa ja 96-70 mol-%:a lineaarista ja/tai haaroittunutta yksiarvoista karboksylihappoa (ks. taulukko 4).

Kuten yllä todettiin ovat HPHP:n kompleksiesterit kuten myös HPHP:n ja jonkin toisen polyoli seoksen kompleksiesterit ovat jo sellaisinaan uusia tuotteita, joita voidaan käyttää voiteluaineekoostumuksissa eri tarkoituksesta varten. Esterit toimivat näiden koostumusten perusöljyinä, jolloin koostumuksissa käytetään tavallisesti lisääinetta (0 - 20 paino-%), joiden tehtäväänä on modifioida koostumuksia niin, että ne soveltuват paremmin eri käyttötarkoitukiin. Niinpä ne soveltuvat jäähdynestekostumusten lisäksi kaikkiin johdannossa mainittuihin voiteluainesovelluksiin.

Esimerkkinä tyypillisistä lisääineista mainittakoon seuraavat: antioksidantit, kulumisenestoaineet, detergentit, vaahdonestoaineet ja korroosionsuoja-aineet.

Sopivista antioksidanteista voidaan mainita fenolit, kuten 2,6-di-t-butylyli-4-metyylifenoli ja 4,4'-metyyleeni-bis(2,6-di-t-butylylifenoli); aromaattiset amiinit, kuten p,p-dioktyylifenyyliamini, mono-oktyylidifenyliamiini, fenotiatsiini, 3,7-dioktyylifenotiatsiini, fenyli-1-naftyyliamiini, fenyli-2-naftyyliamiini, alkyylifenyyli-I-naftalamiinit ja alkyylifenyyli-2-naftalamiinit, sekä rikkipitoiset yhdisteet, kuten ditiofosfaatit, fosfiitit, sulfidit ja ditiometallisuolet, kuten bentsotiatsoli, tina-dialkyyliditiofosfaatit ja sinkki-diaryyliditiofosfaatit.

Sopivia kulumisenestoaineista ovat esim. fosfaatit, fosfaattiesterit, fosfiitit, tiofosfiitit, kuten sinkki-dialkyyliditiofosfaatit, sinkki-diaryyliditiofosfaatit, trikresyylifosfaatit, kloratut vahat, faktisoidut rasvat ja olefiinit, kuten tiolipropionihipappoesterit, dialkyylisulfidit, dibentsyylisulfidit, dialkyylipolysulfidit, alkyylimerkaptaanit, dibentsentiofeenit ja 2,2'-ditiobis(netsotiatsoli); orgaaniset lyijy-yhdisteet, rasvahapot, molybdeenikompleksit, kuten molybdeenisulfidi, halogeenisubstituoidut orgaaniset piiyhdisteet, boraatit ja halogeensubstituoidut fosforiyhdisteet.

Esimerkkinä sopivasta detergenteistä mainittakoon sulfonaatit, aromaattiset sulfonihapot, jotka on substituoitu alkyyleillä, joilla on pitkä ketju, fosfonaatit, tiofosfonaatit, fenolaatit, alkyylifenolien metallisuolet sekä alkyylisulfidit.

Tyypillisiä vaahdonestoaineita ovat silikoniöljyt, esim. dimetyylipolysiloksaanit, ja organosilikaatit, kuten dietyylisilikaatit.

Korroosionestoaineiden esimerkkejä ovat orgaaniset hapot, amiinit, fosfaatit, alkoholit, sulfonaatit ja fosfiitit.

Keksinnön mukaiset esteri valmistetaan tavanomaisella esterointireaktiolla, jossa polyoli tai polyolien seos saatetaan reagoimaan hapon, happoanhydridin tai näiden seoksen kanssa.

Keksinnön kannalta sopivia esterointikatalyytteja ovat erilaiset hapot, kuten rikkihappo, suolahappo, p-tolueenisulfonihappo, butyylititanaatti, tinaokside jne.

Reaktiovaiheessa polyoli tai polyolien seos saatetaan reagoimaan happokomponenttien kanssa käyttämällä happylimääärää (0-10 mooli-%), edullisesti noin 0,1-5 mooli-%, erityisen edullisesti noin 1 mooli-%. Reaktiolämpötila on 150 - 230 °C, edullisesti 170 - 220 °C ja erityisen edullisesti noin 190 - 210 °C.

Esterointi voidaan suorittaa panos- tai puolipanosreaktiolla esimerkiksi siten, että loput haposta lisätään myöhemmin. Tyypillisimmillään esterointi suoritetaan sulatilassa, mutta hiilivetytyppisen väliaineen, kuten tolueenin tai ksyleenin, käyttö on mahdollista. Tuote neutraloidaan joko perinteisiä emäksiä (NaOH, NaHCO₃, Na₂CO₃ jne.) tai orgaanisia amiineja käyttämällä ja pestään. Esterituotteen puhtausaste on edullisesti yli 85 %, etenkin yli 90 % ja esterin happoluku on sopivimman alle 0,1 mg KOH/g.

Seuraavat esimerkit havainnollistavat keksintöä. Ne eivät kuitenkaan rajoita keksinnön suoja- ja suojapiiriä.

Esimerkki 1

Esterien liukoisuuden määritys

Liukoisuus fluorattuihin hiilivetyihin määritetään seuraavasti: 1 ml testattavaa esteriä mitataan koeputkeen ja suljetaan korkki. Koeputki asetetaan kylmähauteseen -30 °C:n lämpötilaan. Kun koeputken ja esterin lämpötila on asettunut -30 °C (noin 5 minuutin kuluttua), fluorattuajähdysainetta, kuten R-134a, lisätään siten, että seoksen kokonaistilavuus on 10 ml.

Esteri-kylmäaineeseoksen annetaan seistä hauteessa -30 °C:n lämpötilassa mahdollisesti

välillä kevyesti sekoittaen. Noin 15 minuutin kuluttua seosta tarkastellaan silmämäärisesti ja havainnoidaan, onko seos yhdessä vai kahdessa faasissa. Mikäli esteri ja jäähdytys muodostavat yhden faasin, esteri liukenee täysin jäähdytysaineeseen. Mikäli seoksessa on kaksi faasia, esteri on joko osittain tai täysin liukenematon jäähdytysaineeseen.

5

Esimerkki 2

HPHP esterien valmistus

10 HPHP esterien valmistusta on kuvattu seuraavassa käyttämällä HPHP:n ja heptaanihapon esteriä esimerkkinä.

15 Raaka-aineet punnittiin lasikolviin seuraavan ohjeen mukaan: HPHP 50 g ja heptaanihappo 64,4 g. Katalyyttinä käytettiin 0,17 g tinaoksidia. Esteröinti suoritettiin sekoittaen sähkömoottorisekoittajalla ja typettäen reaktioseosta noin 210 °C:ssa. Reaktio oli edennyt lopun 7 tunnissa.

20 Tinaoksideista poistettiin tuotteesta suodattamalla. Reaktioseoksesta neutraloitiin happyli-määrä 2 - 5 paino-%:lla trietyyliamiinia. Neutralointi suoritettiin noin 80 °C:ssa ja se kesti 3 tuntia. Reaktioseokseen lisättiin 2 - 5 p-%:a lämmintä vettä ja sekoitettiin varovasti. Reaktioseoksessa liuottimena käytettiin heptaania. Mahdollisesti muodostunut amiinikarboksylihapon suola tai kompleksi erotettiin. Liuotin ja reagoimaton trietyyliamiini poistettiin vakuumitislaamalla. Loppituote suodatettiin. Tulokset on kerätty taulukkoon 1.

25 **Taulukko 1. HPHP:n polyoliesteri**

Näyte	Polyoli	Hapot (mol-%)	V₄₀	V₁₀₀	VI	JP(°C)	Liukoisuus	
							R-134a:han	-30 °C
1	HPHP	Hep-taanihappo (100)	11,63	2,98	111	-	Erinomainen	Erinomainen

Esimerkki 3**HPHP esterien valmistus asyklisistä hoppoanhydrideistä**

HPHP esterien valmistusta on kuvattu seuraavassa käyttämällä HPHP:n ja isovoihappoanhydridin esteriä esimerkkinä.

Raaka-aineet punnittiin lasikolviin seuraavan ohjeen mukaan: HPHP 17,5 g ja isovoihappoanhydridi 19,36 g. Katalyytinä käytettiin 0,37 g metaanisulfonihappoa. Esteröinti suoritettiin lisäämällä anhydridi ja katalyytti tiputussupilosta HPHP:n sekä 2 tunnin aikana, jonka jälkeen reaktioesta sekotettiin noin 150 °C:ssa 2 tuntia.

Reaktioesta neutraloitiin happoylimääärä ja katalyytti pesemällä tuotetta erotussupilossa 3 x 25 ml 5 %:lla natriumkarbonaattiliuoksella ja 3 x 25 ml:lla vettä. Mahdollisesti muodostut karboksyylihapon natriumsuola tai kompleksi erottetiin. Lopuksi tuote kuivattiin natriumsulfaatilla ja suodattiin. Muita estereitä valmistettiin sopivasti olosuhteita muuttamalla. Tulokset on kerätty taulukkoon 2.

Taulukko 2. HPHP:n hoppoanhydriesterit

Näyte	Polyoli	Anhydridi (mol-%)	V ₄₀	V ₁₀₀	VI	Liukoisuus	
						R-134a:han -30 °C	-50 °C
2	HPHP	Isovoihappoanhydridi	7,44	2,14	82	Erinomainen	
3	HPHP	2-etyylibutaanihappoanhydridi	11,84	2,79	64	Erinomainen	Erinomainen

Esimerkki 4**HPHP kompleksiesterien valmistus**

HPHP kompleksiesterien valmistusta kuvataan käyttämällä HPHP:n, oktaanihapon ja adipiinihapon esteriä esimerkkinä.

Raaka-aineet punnittiin lasikolviin seuraavan ohjeen mukaan: HPHP 100 g, oktaanihappo

94,8 g ja adipiinihappo 24,0 g. Katalyyttinä käytettiin 0,328 g tinaoksidia. Esteröinti suoritettiin sekoittaen ja typettäen reaktioseosta noin 210 °C:ssa. Reaktio oli edennyt loppuun 7 tunnissa.

- 5 Reaktioseoksesta neutraloitiin happyylimääät 5 paino-%:lla trietyyliamiinia. Neutralointi suoritettiin noin 80 °C:ssa ja se kesti 3 tuntia. Reaktioseokseen lisättiin 5 p-%:a lämmintää vettä ja sekoitettiin varovasti. Mahdollisesti muodostut amiinikarboksyylihapon suola tai kompleksi erotettiin. Tämän jälkeen reaktioeos pestiin laimealla mineraalihapolla (1 molaarinen H_3PO_4) ja sen jälkeen pestiin 1-2 kertaa lämpimällä vedellä. Lopuksi tuote 10 kuivattiin natriumsulfaatilla ja suodatettiin. Muita kompleksiesteritä valmistettiin sopivasti olosuhteita muuttamalla. Tulokset on kerätty taulukkoon 3.

Taulukko 3. HPHP:n kompleksiesterit

Näyte	Polyoli	Hapot (mol-%)	V_{40}	V_{100}	VI	JP (°C)	Liukoisuus	
							R-134a:han	
							-30 °C	-50 °C
15	4	HPHP	C ₈ (80) AA (20)	39,8	7,06	140	-51	Hyvä
	5	HPHP	C ₈ (80) SA (20)	50,5	8,75	154	-51	Erinomai- nen
								Erinomai- nen

AA = adipiinihappo

SA = sebasiinihappo

C₈ = oktaanihappo

20

Esimerkki 5

HPHP:n polyoli/kompleksiesterien valmistus

- 25 Esimerkin 4 menetelmää noudattamalla valmistettiin HPHP:n ja eräiden muiden polyolien muodostamien seosten kompleksiesterit. Tulokset on esitetty taulukossa 4.

Taulukko 4. HPHP:n polyoli/kompleksi esterit

	Näyte	Polyoli (mol-%)	Hapot (mol-%)	V ₄₀	V ₁₀₀	VI	JP (°C)	Liukoisuus R-134a:han	
								-30 °C	-50 °C
5	6	HPHP(60) BEPD (40)	C ₈ (90) AA (10)	19,78	4,32	128	-63	Tyydyt- tävä	
	7	HPHP (60) BEPD (40)	C ₈ (80) AA (20)	33,20	6,15	136	-54	Hyvä	
	8	HPHP (90) BEPD (10)	C ₈ (90) AA (10)	21,57	4,61	133	-60	Erinomai- nen	Erinomai- nen
	9	HPHP (60) NPG (40)	C ₈ (80) AA (20)	23,69	5,06	147	-63	Erinomai- nen	
10	10	HPHP (90) BEPD (10)	C ₈ (80) AA (20)	32,83	6,14	137	-60	Erinomai- nen	

BEPD = 2-butyili-2-etyyli-1,3-propaanidioli, NPG = neopentyliglykoli

Patenttivaatimukset:

1. Jäähdytysaineseos, joka käsittää kloorittoman fluorihiilivetypohjaisen jäähdytysaineen sekä siihen sekoittuneen, polyoliesteriä sisältävän voiteluaineen, t u n n e t t u siitä, että polyoliesteri koostuu oleellisesti kokonaan 3-hydroksi-2,2-dimetyylipropyli-3-hydroksi-2,2-dimetyylipropionaatin esteristä.

2. Patenttivaatimuksen 1 mukainen jäähdytysaineseos, t u n n e t t u siitä, että polyoliesteri koostuu yli 95 mooli-%:sesti 3-hydroksi-2,2-dimetyylipropyli-3-hydroksi-2,2-dimetyylipropionaatin esteristä.

3. Jäähdytysaineseos, joka käsittää kloorittoman fluorihiilivetypohjaisen jäähdytysaineen sekä siihen sekoittuneen, polyoliesteriä sisältävän voiteluaineen, t u n n e t t u siitä, että polyoliesteri käsittää 3-hydroksi-2,2-dimetyylipropyli-3-hydroksi-2,2-dimetyylipropionaatin esterin sekä trimetylolipropaanin, trimetylolietaanin, pentaerytritolin tai 2,2,4-trimetyylipentadiolin esterin seoksen.

4. Patenttivaatimuksen 3 mukainen jäähdytysaineseos, t u n n e t t u siitä, että 3-hydroksi-2,2-dimetyylipropyli-3-hydroksi-2,2-dimetyylipropionaatin mooliosuus on 50 - 100 %.

5. Jäähdytysaineseos, joka käsittää kloorittoman fluorihiilivetypohjaisen jäähdytysaineen sekä siihen sekoittuneen, polyoliesteriä sisältävän voiteluaineen, t u n n e t t u siitä, että polyoliesteri käsittää 3-hydroksi-2,2-dimetyylipropyli-3-hydroksi-2,2-dimetyylipropionaatin esterin ja 2-butylyli-2-etyyli-1,3-propaanidiolin esterin seoksen.

6. Patenttivaatimuksen 5 mukainen seos, t u n n e t t u siitä, että 2-butylyli-2-etyyli-1,3-propaanidiolin ja 3-hydroksi-2,2-dimetyylipropyli-3-hydroksi-2,2-dimetyylipropionaatin moolisuhde on 5:95 - 99:1.

7. Jäähdytysaineseos, joka käsittää kloorittoman fluorihiilivetypohjaisen jäähdytysaineen sekä siihen sekoittuneen, polyoliesteriä sisältävän voiteluaineen, t u n n e t t u siitä, että polyoliesteri käsittää 3-hydroksi-2,2-dimetyylipropyli-3-hydroksi-2,2-dimetyylipropionaatin esterin ja neopentylyliglykolin, 2-etyyli-1,3-heksaanidiolin tai 1,4-dimetylolisykloheksaanin polyoliesterin seoksen.

8. Jonkin patenttivaatimuksen 3 - 7 mukainen jäähdytysaineseos, t u n n e t t u siitä, että

polyoliesterien seos on valmistettu *in situ*.

9. Jonkin edellisen patenttivaatimuksen mukainen jäähdytysaineseos, tunnettua siitä, että polyoliesterin karboksylyihappotähde on peräisin lineaarisesta tai haaroittuneesta C₄-C₁₈ karboksylyihaposta tai tämän anhydridistä, tai se on peräisin lineaaristen tai haaroittuneiden C₄-C₁₈-karboksylyihappojen tai näiden anhydridien seoksesta.

10. Patenttivaatimuksen 9 mukainen jäähdytysaineseos, tunnettua siitä, että karboksylyihappotähde on peräisin 2-etyyliheksaanihaposta, heptaanihaposta, oktaanihaposta ja/tai lauriinihaposta.

11. Patenttivaatimuksen 1 mukainen jäähdytysaineseos, tunnettua siitä, että esterin karboksylyihappotähde on peräisin yksi- ja kaksiemäksisten karboksylyihappojen seoksesta.

12. Patenttivaatimuksen 11 mukainen jäähdytysaineseos, tunnettua siitä, että yksiarvoinen karboksylyihappotähde on peräisin lineaarisista tai haaroittuneista C₄-C₁₈-karboksylyihapoista, näiden anhydrideistä tai seoksista.

13. Patenttivaatimuksen 11 tai 12 mukainen jäähdytysaineseos, tunnettua siitä, että kaksi-arvoisen karboksylyihappotähde on peräisin oksaalihaposta, malonihaposta, dimetyylimalonihaposta, meripihkahaposta, glutaarihaposta, adipiinihaposta, sebasiinihaposta, pimeliinihaposta, suberiinihaposta tai atselaiinihaposta, tai syklisestä anhydridistä kuten meripihkahappoanhydridistä tai sen aikyylijohdannaisesta, tai trimellitiinianhydridistä.

14. Jonkin patenttivaatimuksen 11 - 13 mukainen jäähdytysaineseos, tunnettua siitä, että yksi- ja kaksiemäksisten karboksylyihappojen moolisuhde seoksessa on 50:50 - 95:5.

15. Jonkin edellisen patenttivaatimuksen mukainen jäähdytysaineseos, tunnettua siitä, että fluorattu hiilivetypohjainen-jäähdytysneste on fluorihiilivety 134, fluorihiilivety 134a, fluorihiilivety 143, fluorihiilivety 143a, fluorihiilivety 152 tai fluorihiilivety 152a tai fluorihiilivetyjen seos.

16. 3-hydroksi-2,2-dimetylipropyli-3-hydroksi-2,2-dimetylipropionaatin kompleksiesterit, jotka sisältävät sen yksi- että kaksiemäksisten karboksylyihappojen tähkeitä.

17. Patenttivaatimuksen 16 mukaiset esterit, t u n n e t u t siitä, että esterien yksiarvoiset karboksylihappotähheet ovat peräisin lineaarisista tai haaroittuneista C₄-C₁₈-karboksylihapoista, näiden anhydrideistä tai seoksista.
- 5 18. Patenttivaatimuksen 16 tai 17 mukaiset esterit, t u n n e t u t siitä, että esterien kak-siarvoiset karboksylihappotähheet ovat peräisin oksaalihaposta, malonihaposta, dimetyylimalonihaposta, meripihkahaposta, glutaarihaposta, adipiinihaposta, sebasiiniha-posta, pimeliinihaposta, suberiinihaposta tai atselaiinihaposta, tai syklisestä anhydridistä, kuten meripihkahappoanhydridistä tai sen alkyyljohdannaisesta, tai trimellitiinianhydri-distä.
- 10 19. Jonkin patenttivaatimuksen 16 - 18 mukaiset esterit, t u n n e t u t siitä, että yksi- ja kaksiemäksisten karboksylihappotähteiden moolisuhde esterissä on 50:50 - 95:5.
- 15 20. Jonkin patenttivaatimuksen 16 - 19 mukaiset esterit, t u n n e t u t siitä, että ne ovat seoksessa jonkin toisen polyolin esterien ja/tai kompleksiesterien kanssa.
21. Patenttivaatimuksen 20 mukaiset esterit, t u n n e t u t siitä, että ne ovat seoksessa NPG:n tai BEPD:n esterien ja/tai kompleksiesterien kanssa.
- 20 22. Jonkin patenttivaatimuksen 16 - 21 mukaisen esterin käyttö voiteluaineiden perusöl-jynä.

(57) Tiivistelmä

Keksintö koskee jäähdytysaineeseosta, joka käsittää kloorittoman fluorihiilivetypohjaisen jäähdytysaineen sekä siihen sekoitteen, polyoliesteriä sisältävän voiteluaineen.

5 Keksinnön mukaan polyoliesteri käsittää 3-hydroksi-2,2-dimetyylipropyyli-3-hydroksi-2,2-dimetyylipropionaatin esterin, jonka kar-

10 boksylihappotähde on peräisin lineaarisesta tai haaroittuneesta C₄-C₁₈-karboksylihaposta tai tämän anhydridistä, tai se on peräisin lineaaristen tai haaroittuneiden C₄-C₁₈-karboksylihappojen tai näiden anhydridien

15 seoksesta. Keksintö koskee myös uusia 3-hydroksi-2,2-dimetyylipropyyli-3-hydroksi-2,2-dimetyylipropionaatin kompleksiestereitä, jotka sisältävät sen yksi- että kaksiemäk-sisten karboksylihappojen tähteitä. Uusilla

20 estereillä on hyvä liukoisuus fluorihiilivetyihin ja erinomaiset voiteluaineominaisuudet.

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(54) Title: POLYOL AND COMPLEX ESTERS FOR USE WITH, IN PARTICULAR, FLUORINATED REFRIGERANTS

(57) Abstract

The invention concerns a refrigerant composition which comprises a chlorine-free hydrofluorocarbon based refrigerant and, mixed with the refrigerant, a lubricant comprising a polyol ester. According to the invention the polyol ester comprises an ester of 3-hydroxy-2,2-dimethylpropyl-3-hydroxy-2,2-dimethylpropionate, the carboxylic acid residue of which is derived from a linear or branched C₄...C₁₈-carboxylic acid or an anhydride thereof, or it is derived from a mixture of linear or branched C₄...C₁₈-carboxylic acids or anhydrides thereof. The present invention also concerns novel complex ester of 3-hydroxy-2,2-dimethylpropyl-3-hydroxy-2,2-dimethylpropionate, which contain residues of mono- or bivalent carboxylic acids. The novel esters exhibit good solubility in fluorinated hydrocarbons and excellent lubricating properties.

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Polyol and complex esters for use with, in particular, fluorinated refrigerants

The present invention concerns a refrigerant compositions according to the preambles of claims 1, 3, 5 and 7. Compositions of this kind generally contain a non-chlorinated hydrofluorocarbon based refrigerant composition together with a polyol ester based lubricant mixed therewith.

The invention also concerns complex esters according to claim 16 and the use thereof in lubricants.

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Lately, as a result of development in many fields of application, the evolution of polyolester type lubricants has been rapid. These products can be used as such or mixed with another base oil, such as a hydrocarbon, in engine oils for automotives, in aeroplane and gas turbine oils, as biodegradable hydraulic oils, as metal working oils and as compressor oils. These products are used in particular together with fluorinated refrigerants as a soluble lubricant component in refrigeration compressors due to their advantageous solubility properties, good technical stability and good cold properties.

The use of, e.g., neopentylglycol and pentaerytritol esters together with refrigerants has been generally suggested. Although these known esters in principle exhibit good lubricant properties, their solubility in non-chlorinated hydrofluorocarbons is often only fair. For this reason they do not work well enough in refrigerant compositions containing fluorinated hydrocarbons.

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It is an object of the present invention to eliminate the problems of the prior art and to provide polyol and complex esters of a novel kind which can be used in particular together with fluorinated refrigerant liquids as lubricants. It is another object of the invention to provide novel esters which are generally suited to the use as base oils of lubricants.

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The present invention is based on the finding that polyol or complex esters of 3-hydroxy-2,2-methyl-3-hydroxy-2,2-dimethylpropionate, i.e. hydroxypivalyl hydroxypivalate, which have good lubricant properties, also exhibit a good or excellent solubility in fluorinated refrigerants and they are therefore suitable for use in refrigerant compositions containing this kind of refrigerants. In particular the polyol esters used comprise the polyol HPHP (hydroxypivalyl hydroxypivalate) as such or together with another polyol, such as NPG, BEPD, ETHD, TMP, TME or PE and the carboxylic acid is a linear or branched C₅ - C₁₈

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monocarboxylic acid or a hydroxy acid, such as hydroxypivalic acid or a mixture of mono- and dicarboxylic acids, such as adipic acid, sebasic acid, azelaic acid, dimethylmalonic acid or cyclic anhydrides.

- 5 More specifically, the refrigerant composition according to the present invention is mainly characterized by what is stated in the characterizing parts of claims 1, 3, 5 and 7.

Complex esters of HPHP are novel and useful as base oils of lubricant oils. The novel esters are characterized by what is stated in the characterizing part of claim 16.

10

The present invention provides considerable advantages. Thus, as mentioned above, the esters of HPHP have good lubricant properties and good solubility in HFC compounds used as refrigerants. The raw materials of said oils can be produced by the economically advantageous oxo-process (hydroformulation). The properties of the oils can easily be

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modified depending on the application by varying the ratio of the polyols of the ester (the amount of HPHP can be 100 to 5 mol-% of the total amount of polyol), the esterifying carboxylic acid and/or the ratio between the esterifying carboxylic acids. By using branched acids the solubility can be improved and by using dibasic acids the viscosity can be raised.

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In the following, the invention will be examined with the aid of a detailed description and using a number of working examples.

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The present esters comprise polyol or complex esters of 3-hydroxy-2,2-methyl-3-hydroxy-2,2-dimethylpropionate. "Polyol ester" means i.a. esters having a carboxylic group comprising a monobasic acid or an anhydride thereof. For the purpose of the present invention, the term "polyol ester" comprises generally also "complex esters" which are esters in which at least a part of the esterifying acids are dibasic. Usually both carboxylic groups of these acids react with an alcohol and yield oligomeric ester compounds, which contain at least two alkohol residues and one carboxylic acid residue. Complex esters also include esters having the carboxylic acid residue formed by a hydroxy acid containing both a hydroxyl group and a carboxylic group. The carboxylic group reacts with the polyol, whereas the hydroxyl group reacts with the carboxylic group of another carboxylic acid.

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35 "Polyol" stands for a compound with at least two hydroxy groups. According to the present invention HPHP can be esterified alone or together with another polyol. These polyols are,

e.g., NPG (neopentylglycol), BEPD (2-butyl-2-ethyl-1,3-propanediol), ETHD (2-ethyl-1,3-hexanediol), TMP (trimethylol propane), TME (trimethylol ethane), PE (pentaerythritol), TMPD (2,2,4-trimethyl-pentanediol) and CHDM (1,4-dimethylol-cyclohexane). Of these polyols chemically and technically stable polyols, containing no hydrogen in the carbon in position 2 or which are (sterically) strongly hindered, such as NPG, ETHD, CHDM and BEPD, are particularly preferred.

Preferably the polyol ester mixtures are formed by mixing the polyols together and by esterifying the thus formed mixture *in situ*.

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According to a first preferred embodiment of the invention, a refrigerant composition is provided, comprising a polyol ester which completely or almost completely (95 mol-%, or even 100 %) consists of an ester of HPHP.

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According to a second preferred embodiment of the present invention, a refrigerant composition is provided, comprising in addition to a polyol ester of HPHP an ester of TMP, TME, PE or TMPD at any ratio. Preferably HPHP forms the main part of the polyol residue of the ester mixture, i.e. its molar amount is 50 % - 100 %.

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According to a third preferred embodiment of the present invention, a refrigerant composition is provided, comprising in addition to a polyol ester of HPHP a polyol ester of BEPD, the molar ratio between BEPD and HPHP being 5:95 to 99:1.

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According to a fourth preferred embodiment of the present invention, a refrigerant composition is provided, comprising in addition to a polyol ester of HPHP a polyol ester of NPG, ETHD or CHDM.

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HPHP or a mixture of HPHP and some other polyol is esterified with a linear or branched C₄ to C₁₈ carboxylic acid or an anhydride thereof. As specific examples of aliphatic, linear or branched, saturated or unsaturated C₄-C₁₈-carboxylic acids which can be used for preparing the ester, the following can be mentioned:

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I saturated, linear C₄-C₁₈-carboxylic acids: butanoic acid (butyric acid), pentanoic acid (valeric acid), hexanoic acid (caproic acid), heptanoic acid, octanoic acid (caprylic acid), decanoic acid (capric acid), dodecanoic acid (lauric acid) and hexadecanoic acid (palmitic acid) and mixtures thereof;

- II saturated, branched C₄-C₁₆-carboxylic acids: isobutanoic acid, 2-ethylhexanoic acid, isononanoic acid and 3,5,5-trimethylhexanoic acid;
- III unsaturated, linear C₄-C₁₈-carboxylic acids: 3-butenoic acid (vinylacetic acid); and
- IV unsaturated, branched C₄-C₁₈-carboxylic acids.

5

In the mixed esters the ratios between the various linear and branched carboxylic acids can vary within large boundaries. Typically, the linear carboxylic acid(s) is (are) present in amounts of 1 to 100 mol-%, preferably about 10 to 90 mol-% of the amount of carboxylic acids. Correspondingly, the amount of branched carboxylic acids is 99 to 1 mol-%, preferably about 90 to 10 mol-%. In particular it is possible to prepare polyesters, which contain 10 to 50 mol-% of at least one linear carboxylic acid and 90 to 50 mol-% of a branched carboxylic acid.

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When polyol esters of HPHP are prepared it is preferred to select linear or branched acids containing 4 to 14 carbon atoms as esterifying carboxylic acid. Octanoic acid, 2-ethylhexanoic acid and lauric acid can be mentioned as examples.

15

Esterifying hydroxy acids are, e.g., hydroxypivalic acid (HPAA), lactic acid, citric acid and dimethylolepropionic acid (DMPA).

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In addition to the afore-mentioned, the esterifying carboxylic acid used can comprise dibasic carboxylic acids, such as oxalic acid, malonic acid, dimethylmalonic acid, succinic acid, glutaric acid, adipic acid, sebacic acid, pimelic acid, suberic acid and azelaic acid. It is also possible to use cyclic anhydrides, such as succinic anhydride or alkyl derivatives thereof, or trimellitic anhydride. Small amounts of aromatic anhydrides, such as phthalic anhydride are also possible.

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The degree of esterification of the polyols is 50 to 100 %, preferably as high as possible, at least about 90 %. In the complex esters the ratio between the mono- and dibasic carboxylic acids is 50 : 50 to 99 : 1.

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The polyol esters/mixed esters/complex esters of HPHP or HPHP and at least another polyol can be used for preparing refrigerant compositions. These contain as a refrigerant one or several chlorine-free hydrofluorocarbon(s) (a refrigerant) in which the ester is dissolved. As specific examples of the refrigerant liquid component of the compositions, the following can be mentioned: hydrofluorocarbon 134 (1,1,2,2-tetrafluoroethane),

hydrofluorocarbon 134a, hydrofluorocarbon 143 (1,1,2-trifluoroethane), hydrofluorocarbon 143a (1,1,1-trifluoroethane), hydrofluorocarbon 152 (1,2-difluoroethane) and hydrofluorocarbon 152a (1,1-difluoroethane). Of these compounds, hydrofluorocarbon 134a is generally preferred. Mixtures of hydrofluorocarbons can also be employed.

5 Examples include hydrofluorocarbon mixture 407 (mixture of hydrocarbons 32, 125 and 134a) and hydrofluorocarbon mixture 410 (mixture of hydrocarbon 32 and 125).

Depending on application, the viscosity requirement for the ester is, according to ISO-standard, between 5 and 200 cSt (40 °C). Low (5 - 10) and intermediate (22 - 32) viscosities are needed for, e.g., refrigerators and other small refrigeration devices. High 10 viscosity (46 - 68) compositions are used for, e.g., cooling equipment of air conditioners.

As already mentioned in the beginning, the viscosity of the prepared esters can be adjusted as desired by suitably selecting esterifying carboxylic acid components and/or by adding a 15 further polyol to the BEPD. Thus, by using conventional linear or branched carboxylic acids (C₄ - C₁₂) and, e.g., adipic acid, it is possible to prepare esters having viscosities in the range of about 15-22 cSt at 40 °C. Their viscosity indeces are about 100 and pour points below -40 °C. They are suitable for use in smallish cooling equipment. By increasing the amount of a branched carboxylic acid it is possible to increase the solubility 20 of the esters. By feeding a dibasic carboxylic acid into the esterification reaction and in particular by using it together with linear or branched acids, the viscosity of the product can be increased. The cold properties and good solubility remain. Mixing HPHP with another polyol before esterification makes it possible to increase even further without impairing the solubility . The viscosity increase to the range of high viscosity.

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As examples of particularly valuable esters, the following can be mentioned:

- I Polyol esters of HPHP, which contain 30 to 60 % linear carboxylic acid and 70 to 30 40 mol-% branched carboxylic acid
- II Complex esters of HPHP which contain 1 to 10 mol-% dibasic carboxylic acid and 90 to 99 mol-% linear and/or branched monobasic carboxylic acid; and
- III Complex esters of HPHP and NPG/BEPD, which contain 4 to 30 mol-% dibasic carboxylic acid and 96 to 70 mol-% linear and/or branched monobasic carboxylic acid.

35

As mentioned above, the complex esters of HPHP as well as complex esters of HPHP and

some other polyol, are already as such novel products which can be used in lubricant compositions for different aims. The esters work as base oil of these compositions and additives are usually employed in amounts of 0 to 20 wt.-% in the compositions for the purpose of modifying the compositions such that they are better suited for various 5 applications. Thus, the esters are suitable not only for use in refrigerant compositions but also for all applications mentioned in the introduction of the specification.

Conventional additives which can be used in the refrigerant liquid compositions include, e.g., the following: antioxidants, antiwear agents, detergents, defoaming agents and 10 corrosion inhibitors.

Suitable antioxidants include phenols, such as 2,6-di-t-butyl-4-methylphenol and 4,4'-methylene-bis(2,6-di-t-butylphenol); aromatic amines, such as p,p-dioctylphenylamine, monoocetyl diphenylamine, phenothiazine, 3,7-dioctylphenothiazine, phenyl-1- 15 naphthylamine, phenyl-2-naphthylamine, alkylphenyl-1-naphththalamines and alkyl-phenyl-2-naphthal-amines, as well as sulphur-containing compounds, e.g. dithiophosphates, phosphites, sulphides and dithio metal salts, such as benzothiazole, tin-dialkyldithiophosphates and zinc diaryldithiophosphates.

20 Suitable antiwear agents include, for example, phosphates, phosphate esters, phosphites, thiophosphites, e.g. zinc dialkyl dithiophosphates, zinc diaryldithiophosphates, tricresyl phosphates, chlorinated waxes, sulphurised fats and olefins, such as thiodipropionic esters, dialkyl sulphides, dialkyl polysulphides, alkyl-mercaptanes, dibenzothiophenes and 2,2'-dithiobis(benzothiazole); organic lead compounds, fatty acids, molybdenum complexes, 25 such as molybdenum disulphide, halogen substituted organosilicon compounds, organic silicon compounds, borates and halogen-substituted phosphorus compounds.

As specific examples of suitable detergents, the following should be mentioned: 30 sulphonates, aromatic sulphonic acids, which are substituted with alkyl having a long chain, phosphonates, thiophosphonates, phonolates, metal salts of alkylphenols, and alkyl sulphides.

Typical defoaming agents include silicon oils, e.g. dimethylpolysiloxane and organic silicon compounds such as diethyl silicates.

35 Organic acids, amines, phosphates, alcohols, sulphonates and phosphites are examples of

corrosion inhibitors.

The esters according to the invention are prepared by a conventional esterification reaction wherein a polyol or a mixture of polyols is (are) reacted with an acid mixture in the presence of a catalyst or without a catalyst. Various acids, such as sulphuric acid, hydro-chloric acid, p-toluene sulphonic acid, butyl titanate, tinoxide etc., are suitable catalysts for carrying out the invention. A particularly advantageous catalyst is tin oxide.

During the reaction, the polyol is reacted with the acid component by using an equivalent amount of acid, a deficient amount of acid or a surplus of acid; the excess acid amounts to typically a maximum of 10 mol-%, preferably about 0.1 to 5 mol-%, in particular about 1 mol-%. The reaction temperature is 150 to 230 °C, preferably 170 to 220 °C and in particular about 190 to 210 °C.

The esterification can be carried out as a batch or semibatch process for example by adding the remaining acid later on. The most typical embodiment comprises carrying out esterification in the melt phase but it is also possible to use a hydrocarbon-type medium, such as toluene or xylene. The product is neutralized either with conventional bases (NaOH, NaHCO₃, Na₂CO₃, etc.) or with organic amines and are then washed. The degree of purification of the ester product is preferably over 85 %, in particular over 90 % and the acid number of the ester is preferably below 0.1 mg KOH/g.

The following examples illustrate the invention. They do not, however, limit the scope of the invention.

Example 1

Determination of ester solubility

Solubility in fluorinated hydrocarbons was determined as follows: 1 ml of the studied ester was put into a test tube which was closed with a stopper. The test tube was placed in a cold bath at a temperature of -30 °C. When the temperature of the test tube and the ester had reached -30 °C (after about 5 minutes), a fluorinated refrigerant, such as R-134a, was added to make a total volume of 10 ml.

The ester-refrigerant mixture was allowed to stand in the bath at -30 °C with possibly a light occasional stirring. After about 15 minutes the mixture was visually assessed and it

was determined whether the mixture contained one or two phases. If the ester and the refrigerant liquid formed one phase, the ester is completely dissolved in the refrigerant liquid. If there are two phases present in the mixture, the ester is either partially or completely insoluble in the refrigerant liquid.

5

Example 2

Preparation of esters of HPHP

The preparation of esters of HPHP is described in the following using the esters of HPHP and heptanoic acid as an example.

The raw materials were weighed into a glass bulb according to the following recipe: HPHP 50 g and heptanoic acid 64.6 g. The catalyst used comprised 0.17 g tin oxide. The esterification was carried out by stirring using a mixer with an electric motor and by nitrigating the reaction mixture at about 210 °C. The reaction was complete within 7 hours.

Tin oxide was removed by filtration. Excess acid was neutralized from the reaction mixture with 2 - 5 wt-% triethylamine. The neutralization was carried out at 80 °C for 3 hours.

Warm water (2 - 5 wt-%) was added to the reaction mixture and it was mixed cautiously.

The solvent of the reaction mixture comprised heptane. Any formed aminocarboxylic acid salt or complex was separated. The solvent and the unreacted triethylamine were removed by vacuum distillation. The end product was filtered. The results are summarized in Table 1.

Table 1. Polyol esters of HPHP

Sample	Polyol	Acids (mol-%)	V₄₀	V₁₀₀	VI	PP(°C)	Solubility in	
							R-134a	
							-30 °C	-50 °C
1	HPHP	Heptanoic acid (100)	11.63	2.98	111	-	Excellent	Excellent

30

Example 3**Preparation of esters of HPHP from acyclic anhydrides**

The preparation of esters of HPHP is illustrated by using the preparation of an ester of

5 HPHP and isobutyric anhydride as an example.

The raw materials were weighed into a glass reactor according to the following recipe:

HPHP 17.5 g and isobutyric anhydride 19.36 g. The catalyst used comprised 0.37 g

10 methanesulphonic acid. The esterification was carried out by adding the anhydride and the catalyst from a dropping funnel to the HPHP during 2 hours, and then the reaction mixture was stirred at about 150 °C for 2 hours.

Excess acid was neutralized from the reaction mixture and the catalyst was washed in a separation funnel with 3 x 25 ml 5 % sodium carbonate solution and 3 x 25 ml water. Any

15 sodium salt or complex of the carboxylic acid were separated. Finally, the product was dried on sodium sulphate and filtered. Other esters were prepared by suitable modification of the conditions. The results are summarized in Table 2.

Table 2. Acid anhydride esters of HPHP

Sample	Polyol	Acids (mol-%)	V ₄₀	V ₁₀₀	VI	Solubility in R-134a	
						-30 °C	-50 °C
2	HPHP	Isobutyric anhydride	7.44	2.14	82	Excellent	
3	HPHP	2-ethylbutanoic anhydride	11.84	2.79	64	Excellent	Excellent

Example 4**Preparation of complex esters of HPHP**

Complex esters of HPHP is described using the ester of HPHP, octanoic acid and adipic ester as an example.

The raw materials were weighed into a glass reactor according to the following recipe:

35 HPHP 100 g, octanoic acid 94.8 g and adipic acid 24.0 g. The catalyst used comprised

0.328 g tin oxide. acid. The esterification was carried out by stirring and nitrigating the reaction mixture at about 210 °C. The reaction was complete within 7 hours.

Excess acid was neutralized from the reaction mixture with 5 wt-% triethylamine. The neutralization was carried out at 80 °C for 3 hours. Warm water (5 wt-%) was added to the reaction mixture and it was mixed cautiously. Any formed aminocarboxylic acid salt or complex was separated. The reaction mixture was then washed with a dilute mineral acid (1 molar H₃PO₄) and subsequently 1 to 2 times with warm water. Finally, the product was dried on sodium sulphate and filtered. Other esters were prepared by suitable modification of the conditions. The results are summarized in Table 3.

Table 3. Complex esters of HPHP

Sample	Polyol	Acids (mol-%)	V ₄₀	V ₁₀₀	VI	PP(°C)	Solubility in R-134a	
							-30 °C	-50 °C
4	HPHP	C ₈ (80) AA (20)	39.8	7.06	140	-51	Good	
5	HPHP	C ₈ (80) SA (20)	50.5	8.75	154	-51	Excellent	Excellent

A_A = adipic acid

SA = sebasic acid

C₈ = octanoic acid

Example 5

Preparation of polyol/complex esters of HPHP

Following the process of Example 4 complex esters of mixtures of HPHP and some other polyols were prepared. The results are indicated in Table 4.

Table 4. Polyol/complex esters of HPHP

5	Sample	Polyol	Acids (mol-%)	V ₄₀	V ₁₀₀	VI	PP(°C)	Solubility in R-134a	
								-30 °C	-50 °C
	6	HPHP (60) BEPD (40)	C ₈ (90) AA (10)	19.78	4.32	128	-63	Fair	
	7	HPHP (60) BEPD (40)	C ₈ (80) AA (20)	33.20	6.15	136	-54	Good	
	8	HPHP (90) BEPD (10)	C ₈ (90) AA (10)	21.57	4.61	133	-60	Excellent	Excellent
	9	HPHP (60) NPG (40)	C ₈ (80) AA (20)	23.69	5.06	147	-63	Excellent	
10	10	HPHP (90) BEPD (10)	C ₈ (80) AA (20)	32.83	6.14	137	-60	Excellent	

BEPD = 2-butyl-2-ethyl-1,3-propanediol, NPG = neopentylglycol

Claims:

1. Refrigerant composition comprising a chlorine-free hydrofluorocarbon based refrigerant and, mixed therewith, a lubricant containing a polyol ester, characterized in that the polyol ester comprises essentially totally an ester of 3-hydroxy-2,2-dimethyl-propyl-3-hydroxy-2,2-dimethylpropionate.

2. The refrigerant composition according to claim 1, wherein the polyol ester is to more than 95 mol-% constituted by an ester of 3-hydroxy-2,2-dimethylpropyl-3-hydroxy-2,2-dimethylpropionate.

3. Refrigerant composition comprising a chlorine-free hydrofluorocarbon based refrigerant and, mixed therewith, a lubricant containing a polyol ester, characterized in that the polyol ester comprises a mixture of an ester of 3-hydroxy-2,2-dimethyl-propyl-3-hydroxy-2,2-dimethylpropionate and an ester of trimethylol propane, trimethylol ethane, pentaerythritol or 2,2,4-trimethylpentadiol.

4. The refrigerant composition according to claim 3, wherein the molar ratio of the 3-hydroxy-2,2-dimethyl-propyl-3-hydroxy-2,2-dimethylpropionate is 50 to 100 %.

5. Refrigerant composition comprising a chlorine-free hydrofluorocarbon based refrigerant and, mixed therewith, a lubricant containing a polyol ester, characterized in that the polyol ester comprises a mixture of an ester of 3-hydroxy-2,2-dimethyl-propyl-3-hydroxy-2,2-dimethylpropionate and an ester of 2-butyl-2-ethyl-1,3-propanediol.

6. The refrigerant composition according to claim 5, wherein the molar ratio of the 2-butyl-2-ethyl-1,3-propanediol and the 3-hydroxy-2,2-dimethyl-propyl-3-hydroxy-2,2-dimethylpropionate is 5:95 - 99:1.

7. Refrigerant composition comprising a chlorine-free hydrofluorocarbon based refrigerant and, mixed therewith, a lubricant containing a polyol ester, characterized in that the polyol ester comprises a mixture of an ester of 3-hydroxy-2,2-dimethyl-propyl-3-hydroxy-2,2-dimethylpropionate and a polyol ester of neopentylglycol, 2-ethyl-1,3-hexanediol or 1,4-dimethylol-cyclohexane.

8. The refrigerant composition according to any of claims 3 to 7, wherein the polyol ester

mixture is prepared *in situ*.

9. The refrigerant composition according to any of the preceding claims, wherein
the carboxylic acid residue of the polyol ester is derived from a linear or branched C₄...C₁₈-
5 carboxylic acid, or an anhydrides thereof, or it is derived from a mixture of linear or
branched C₄...C₁₈-carboxylic acids or anhydrides thereof.

10. The refrigerant composition according to claim 9, wherein the carboxylic acid residue
is derived from 2-ethylhexanoic acid, heptanoic acid, octanoic acid and/or lauric acid.

11. The refrigerant composition according to claim 1, wherein the carboxylic acid residue
of the ester is derived from a mixture of mono- and dibasic carboxylic acids.

12. The refrigerant composition according to claim 11, wherein the monobasic carboxylic
15 acid residue is derived from linear or branched C₄...C₁₈-carboxylic acids or anhydrides or
mixtures thereof.

13. The refrigerant composition according to claim 11 or claim 12, wherein the dibasic
carboxylic acid residue is derived from oxalic acid, malonic acid, dimethylmalonic acid,
20 succinic acid, glutaric acid, adipic acid, sebasic acid, pimelic acid, suberic acid or azelaic
acid, or a cyclic anhydride such as succinic anhydride or an alkyl derivative thereof, or
trimellitic anhydride.

25 14. The refrigerant composition according to any of claims 11 to 13, wherein the molar
ratio between the mono- and dibasic carboxylic acids is 50:50 to 95:5.

30 15. The refrigerant composition according to any of the preceding claims, wherein the
fluorinated hydrocarbon based refrigerant is hydrofluorocarbon 134, hydrofluorocarbon
134a, hydrofluorocarbon 143, hydrofluorocarbon 143a, hydrofluorocarbon 152 or
hydrofluorocarbon 152a or a mixture of hydrofluorocarbons.

16. Complex esters of 3-hydroxy-2,2-dimethyl-propyl-3-hydroxy-2,2-dimethylpropionate
which contain residues of both mono- and dibasic carboxylic acids.

35 17. The complex esters according to claim 16, wherein the monobasic carboxylic acid
residues are derived from linear or branched C₄...C₁₈-carboxylic acids or anhydrides or

mixtures thereof.

18. The complex esters according to claim 16 or claim 17, wherein the dibasic carboxylic acid residues are derived from oxalic acid, malonic acid, dimethyl malonic acid, succinic acid, glutaric acid, adipic acid, sebasic acid, pimelic acid, suberic acid or azelaic acid, or a cyclic anhydride such as succinic anhydride or an alkyl derivative thereof, or trimellitic anhydride.

19. The complex esters according to any of claims 16 to 18, wherein the molar ratio between the mono- and dibasic carboxylic acid residues in the ester is 50:50 to 95:5.

20. The complex esters according to any of claims 16 to 19, which are mixed with esters and/or complex esters of another polyol.

15 21. The complex esters according to claim 20, wherein the esters are in a mixture of esters and/or complex esters of NPG or BEPD.

22. The use of an ester according to any of claims 16 to 21 as base oils for lubricants.

INTERNATIONAL SEARCH REPORT

1

International application No.

PCT/FI 98/00329

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C10M 105/42, C09K 5/04, C07C 69/67

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C10M, C09K, C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CA, WPI

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

2

International application No.

PCT/FI 98/00329

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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PCT/FI 98/00329

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(51) International Patent Classification ⁶ : C10M 105/42, C09K 5/04, C07C 69/67		A1	(11) International Publication Number: WO 98/46706 (43) International Publication Date: 22 October 1998 (22.10.98)									
<p>(21) International Application Number: PCT/FI98/00329</p> <p>(22) International Filing Date: 14 April 1998 (14.04.98)</p> <p>(30) Priority Data:</p> <table> <tr> <td>971548</td> <td>11 April 1997 (11.04.97)</td> <td>FI</td> </tr> <tr> <td>971549</td> <td>11 April 1997 (11.04.97)</td> <td>FI</td> </tr> <tr> <td>980730</td> <td>31 March 1998 (31.03.98)</td> <td>FI</td> </tr> </table> <p>(71) Applicant (for all designated States except US): NESTE OY [FI/FI]; Keilaniemi, FIN-02150 Espoo (FI).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): KOISTINEN, Jari [FI/FI]; Lammimutka 2 C 14, FIN-40520 Jyväskylä (FI); RISSANEN, Kari [FI/FI]; Hankamäentie 13, FIN-41520 Hankasalmi (FI). SILVENNOINEN, Laura [FI/FI]; Kilpisenkatu 16 A 20, FIN-40100 Jyväskylä (FI). KOSKIMIES, Salme [FI/FI]; Hämeenapajantie 7, FIN-00850 Helsinki (FI).</p> <p>(74) Agents: LAINE, Seppo et al.; seppo Laine Oy, Lönnrotinkatu 19 A, FIN-00120 Helsinki (FI).</p>		971548	11 April 1997 (11.04.97)	FI	971549	11 April 1997 (11.04.97)	FI	980730	31 March 1998 (31.03.98)	FI	<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published With a revised version of the international search report. In English translation (filed in Finnish).</p> <p>(88) Date of publication of the revised version of the international search report: 29 April 1999 (29.04.99)</p>	
971548	11 April 1997 (11.04.97)	FI										
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980730	31 March 1998 (31.03.98)	FI										

(54) Title: POLYOL AND COMPLEX ESTERS FOR USE WITH, IN PARTICULAR, FLUORINATED REFRIGERANTS

(57) Abstract

The invention concerns a refrigerant composition which comprises a chlorine-free hydrofluorocarbon based refrigerant and, mixed with the refrigerant, a lubricant comprising a polyol ester. According to the invention the polyol ester comprises an ester of 3-hydroxy-2,2-dimethylpropyl-3-hydroxy-2,2-dimethylpropionate, the carboxylic acid residue of which is derived from a linear or branched C₄...C₁₈-carboxylic acid or an anhydride thereof, or it is derived from a mixture of linear or branched C₄...C₁₈-carboxylic acids or anhydrides thereof. The present invention also concerns novel complex ester of 3-hydroxy-2,2-dimethylpropyl-3-hydroxy-2,2-dimethylpropionate, which contain residues of mono- or bivalent carboxylic acids. The novel esters exhibit good solubility in fluorinated hydrocarbons and excellent lubricating properties.

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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C10M 105/42, C09K 5/04, C07C 69/67

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Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 98/00329

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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